



# An effective heterogeneous Ir(III) catalyst, immobilized on a heptazine-based organic framework, for the hydrogenation of CO<sub>2</sub> to formate



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## ABSTRACT

Heterogenized Ir(III) catalysts were synthesized through the formation of coordination bonds between Ir(III) ions and heptazine-based covalent organic frameworks (COFs). The coordination environment of the Ir(III) ion contained the two heptazinyl nitrogen atoms as well as Cp\* and Cl<sup>-</sup> anions. The heterogeneous catalyst exhibits high CO<sub>2</sub> hydrogenation activity (turnover number (TON) = 6400 and turnover frequency (TOF) = 1500 h<sup>-1</sup>). In addition, the sub-micron sized catalyst was easily separated by filtration and the catalytic efficiency of the isolated catalyst was demonstrated over repeated cycles.

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## 1. Introduction

Carbon dioxide is considered to be the main contributor to the greenhouse effect, and hence, its use as an abundant chemical feedstock is of great interest. Accordingly, diverse reactions of CO<sub>2</sub> have been identified, including polymerization and carbonate formation with epoxides, the carboxylation of organic compounds, and hydrogenation [1–4]. In particular, the reduction of CO<sub>2</sub> to CO, formic acid/formates, formaldehyde, methanol and methane has attracted much attention because these products can be employed as basic chemicals and some are even being considered as renewable fuels [5,6]. In particular, the hydrogenation of CO<sub>2</sub> to formic acid/formates merits special attention because formic acid can be regarded as a liquid form of hydrogen, an environmentally acceptable renewable fuel, which is easy to store and transport. Moreover, formic acid/formates are used as basic chemicals in various industries: for example, to control pH in the leather and dyeing industries, as coagulants in the synthesis of rubber, to promote

the fermentation of acetic acid, as preservatives and antibacterial agents in livestock feed and as de-icing agent etc. [7,8].

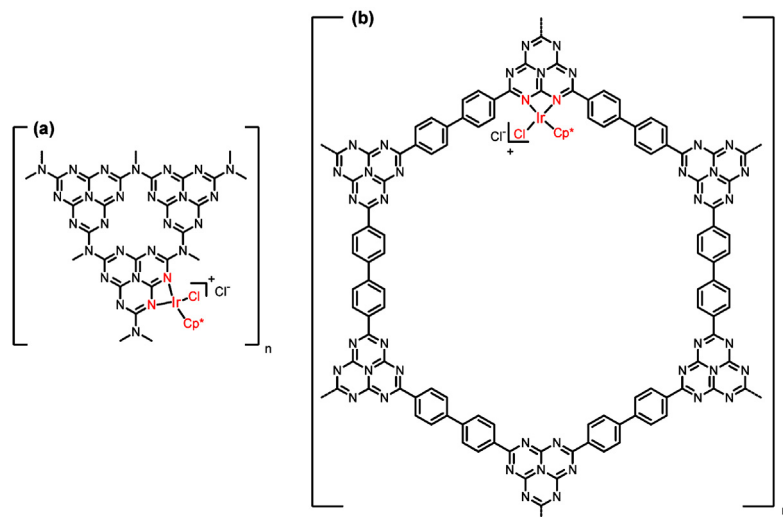
Since the discovery of phosphine-based Ru complexes, excellent progress has been achieved in the development of homogeneous catalysts for the hydrogenation of CO<sub>2</sub> to formate [9–11]. In particular, extensive studies on homogeneous Ir, Ru, and Rh complexes have been reported due to their high activities, and recently, half-sandwich Ir derivatives have shown tremendous catalytic activity in aqueous reaction media, resulting in the production of ca 1.70 M formate [12–15]. Although the reported homogeneous Ir complexes exhibit excellent catalytic efficiency, the industrial realization of these catalysts still poses difficulties owing to the decomposition of the generated formate into CO<sub>2</sub> and H<sub>2</sub> during the subsequent separation step(s). Hence, the commercial production of formic acid still relies on the conventional method of combining carbon monoxide with methanol. Therefore the development of effective heterogeneous catalysts, which would be easily separable from the reaction mixture, would be highly desirable to overcome such drawbacks.

Several approaches have been taken to generate heterogeneous catalysts; these include the immobilization of Ru or Ir complexes on silica or amine-based polymeric supports, and the syntheses of alumina-supported ruthenium hydroxide and

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**Scheme 1.** Structural representations of heterogenized catalysts, **1** (a) and **2** (b).

titanium dioxide-supported gold catalysts [16–19]. Notably, an Ir complex immobilized on the surface of silica particle(s) showed a turnover number (TON) of 2700 (the highest TON reported to date for a heterogeneous catalytic system) [19]. However, the catalytic efficiency of these heterogeneous catalysts is still not as high as those of homogeneous catalyst systems.

Recently, covalent organic frameworks (COFs) with N-donor motifs have attracted much attention as catalyst supports to heterogenize homogenous species through coordination bonds between the frameworks and the metal ions in organometallic complexes [20,21]. In addition, COFs have high stabilities, pore volumes, and high surface areas, making them ideal supports for catalysts [22–24]. Herein, we report the synthesis and catalytic activities of two new, air stable iridium catalysts (**1** and **2**) immobilized on heptazine-based frameworks (HBFs) (Scheme 1). With these catalysts, highly efficient catalytic activity (TON = 6400) for the conversion of CO<sub>2</sub> into formate was obtained under mild conditions.

## 2. Experimental

### 2.1. General

All reagents and chemicals were purchased from commercial supplies and used without further treatment. Lithium bromide, potassium bromide, chlorobenzene (anhydrous), dicyandiamide, potassium hydroxide, triethylamine (Et<sub>3</sub>N) and isopropanol were purchased from Sigma Aldrich. Iridium chloride hydrate, 1,2,3,4,5-pentamethyl cyclopentadiene (Cp\*), and biphenyldicarbonitrile were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). CO<sub>2</sub> (99.99%) and H<sub>2</sub> (99.99%) were purchased from Seoul Specialty Gases Co. Ltd. and used without further purification. [IrCp\*Cl<sub>2</sub>]<sub>2</sub>, [IrCp\*(bipyridine)Cl<sub>2</sub>], graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), and the heptazine-based framework with the biphenyl linker (HBF-2) were synthesized according to reported procedures [25–28].

Scanning Electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements were performed on a JEM-7610F instrument (JEOL Ltd., JAPAN) operated at an accelerating voltage of 20.0 kV. X-ray photoelectron Spectroscopy (XPS) analysis was performed on an ESCA 2000 system (VG Microtech) at a pressure of  $\sim 3 \times 10^{-9}$  mbar using Al K $\alpha$  as an excitation source ( $h\nu = 1486.6$  eV) with a concentric hemispherical analyzer. The iridium content in catalyst **2** was determined by inductively coupled plasma-mass spectroscopy (ICP-MS, iCAP-Q, Thermo Fisher

Scientific). The concentration of formate was analyzed by high performance liquid chromatography (HPLC) on an Aminex HPX-87H column with a refractive index detector using 0.005 M H<sub>2</sub>SO<sub>4</sub> as the eluent.

### 2.2. Synthesis of [IrCp\*(g-C<sub>3</sub>N<sub>4</sub>)Cl<sub>2</sub>] (**1**) and [IrCp\*(HBF-2)Cl<sub>2</sub>] (**2**)

To a solution of [IrCp\*Cl<sub>2</sub>]<sub>2</sub> (0.188 g, 0.236 mmol) in chlorobenzene, g-C<sub>3</sub>N<sub>4</sub> or HBF-2 (0.100 g) was added and heated to reflux for 48 h. The resulting, air stable yellow (for **1**) or black (for **2**) solid was filtered at room temperature, washed with excess methylene chloride (2  $\times$  250 mL), and dried under vacuum.

### 2.3. Representative procedure for the hydrogenation of CO<sub>2</sub> to formate

Hydrogenation was carried out in a 100 mL stainless steel reactor with a glass vessel insert. In a typical reaction, the catalyst (10 mg) was added to an aqueous Et<sub>3</sub>N solution (20 mL) and saturated with CO<sub>2</sub>. The CO<sub>2</sub> and H<sub>2</sub> gases were filled to the desired pressure and heated to 80–200 °C. The reactor was cooled to room temperature after the designated time and the pressure was slowly released. The concentration of the generated formate was analyzed by HPLC using H<sub>2</sub>SO<sub>4</sub> (0.005 M) as the eluent.

In the recycling experiments, the catalyst was recovered by simple filtration, washed with water, and used for further experiments after drying.

## 3. Results and discussion

Recently, COFs have attracted much attention as catalyst supports because of their high thermal stability, pore volumes, and surface areas. The porous two-dimensional sheets-like structures of the COFs may allow the passage and capture of CO<sub>2</sub> and H<sub>2</sub> gases, along with small molecules such as formate. These nitrogen-containing COFs have the additional advantage of forming coordination bonds with metal cations, resulting in the immobilization of organometallic complexes and increased chemical and thermal stabilities. This combination of reasons led us to prepare heterogenized catalysts by the immobilization of IrCp\* moieties on the heptazine-based COFs, g-C<sub>3</sub>N<sub>4</sub> and HBF-2, resulting in the formation of the highly dispersed heterogenized catalysts **1** and **2**, respectively. The synthetic routes for g-C<sub>3</sub>N<sub>4</sub> and HBF-2 are well documented [29–31].

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