Supporting Information

Continuous-flow formic acid production from hydrogenation of CO$_2$ without any base

Zhaofu Zhang,* Shuaishuai Liu, Mingqiang Hou, Guanying Yang and Buxing Han*

E-mail: zhangzf@iccas.ac.cn; hanbx@iccas.ac.cn
Experimental

RuCl₃, Pentamethylcyclopentadienyliridium (III) chloride dimer ([IrCp*Cl₂]₂) were purchased from J&K Co., Ltd. 1,3,5-triaza-7-phosphaadamantane (PTA) was obtained from Aldrich Co., Ltd. Triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt hydrate (TPPTS) was provided by Alfa Aesar Co., Ltd. Sodium diphenylphosphinobenzene-3-sulfonate (TPPMS), 2,2'-Bipyridine-6,6'-dial were purchased from Tci. Co., Ltd. 2,2'-Biimidizoline was obtained from Innochem Co., Ltd. CO₂ (99.999%), H₂ (99.99%) was provided from Beijing Analytical Instrument Company. Other chemicals were supplied by Sinopharm Chemical Reagent Co., Ltd.

The schematic diagram of the optical high-pressure cell of 500 mL is shown in Scheme S1. Semipermeable membrane (anion-exchange membranes AMI 7001 from Ultrex or RO membrane from Dow) is set between the two parts of a Teflon cell, and the two parts were fixed with stainless steel screws. In a typical experiment, certain amounts of catalyst (metal salt and ligand) and water (25 mL) were added in the right side of the Teflon cell. After covered, air in the high-pressure cell was replaced by CO₂ for three times. The high-pressure cell was placed in an air bath of desired temperature, and stirring was continued for 12 hrs to make metal salts and ligands combine. Then H₂ and CO₂ were charged into the high-pressure cell to certain pressure, and the reaction proceeded under stirring. Water was injected into the cell through inlet 1 continually with a liquid pump (Shimadzu LC-20AT), formic acid solution was released continously from the outlet 2. The concentration of formic acid (after degased with a water pump for 20 mintures) was determined by titration with NaOH solution (calibrated with Na₂CO₃ and hydrochloric acid) using phenolphthalein as indicator.

Scheme S1. Schematic diagram of the optical high-pressure cell.
(1) water inlet; (2) formic acid solution outlet; (3) gas inlet; (4) semipermeable membrane; (5) teflon cell; (6) magic stirrer.

The off-line concentrating experiment was conducted in a Teflon cell as shown in Scheme 1a with 20 cm² active membrane surface area, and commercial anion and cation-exchange membranes (AMI 7001 and CMI-7000 from Ultrex) were selected. Copper sheet was used as electrode and copper formate aqueous solution was used as electrolyte in electrode compartments. Formic acid solution was
ejected in the three feed compartments. Concentrated formic acid solution was sucked out with a syringe. Current was kept at 50 mA. The concentration of formic acid solution got was measured as mentioned above and the Faraday efficiency was known from current, time and formic acid obtained.

In the on-line concentration experiment of formic acid, the above electrodialysis cell was put in the optical high-pressure vessel as shown in Scheme S2. 0.25 µmol RuCl₃, 1.1 µmol PTA and 25 mL water were put in one flask and kept stirring for 24 hrs under N₂ atmosphere to make metal salt and ligand combine, then the solution was transferred into the three feed compartments (b, d and f). Copper sheet was used as electrode and copper formate water solution was used as electrolyte in electrode compartments (a and g). After covered, air in the high-pressure cell was replaced by CO₂ for three times. The high-pressure cell was placed in an air bath of desired temperature, and then CO₂ and H₂ were charged into the high-pressure vessel. After reaction for 12 hours, 20 mA current was applied for 2 hrs, and the concentrated formic acid solution in compartments c and e was released out from outlet 2 and 5. The concentration of formic acid got was determined by titration with NaOH solution using phenolphthalein as indicator.

Scheme S2. Schematic diagram of the optical high-pressure cell.
(1) wire; (2) formic acid solution outlet; (3) gas inlet; (4) wire; (5) formic acid solution outlet.