

Electronic Supplementary Information

Automatic high-pressure hydrogen generation from formic acid in the presence of nano-Pd heterogeneous catalysts at mild temperatures

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Chemicals

Graphite (C, 99.8%, Alfa Aesar), potassium permanganate (KMnO_4 , 99.3%, Wako Pure Chemical Industries, Ltd.), sulfuric acid (H_2SO_4 , 95%, Wako Pure Chemical Industries, Ltd.), phosphoric acid (H_3PO_4 , 85%, Wako Pure Chemical Industries, Ltd.), hydrogen peroxide (H_2O_2 , 30%, Wako Pure Chemical Industries, Ltd.), *p*-phenylenediamine (PDA, $\text{C}_6\text{H}_8\text{N}_2$, 97%, Wako Pure Chemical Industries, Ltd.), sodium borohydride (NaBH_4 , 92%, Nacalai Tesque, Inc.), potassium tetrachloropalladate (K_2PdCl_4 , 95%, Wako Pure Chemical Industries, Ltd.), hydrogen tetrachloroaurate(III) tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, 99%, Wako Pure Chemical Industries, Ltd.), formic acid (FA, HCOOH , 98%, Wako Pure Chemical Industries, Ltd.), sodium formate (SF, HCOONa , 98%, Wako Pure Chemical Industries, Ltd.), hydrochloric acid (HCl , 35%, Wako Pure Chemical Industries, Ltd.), nitric acid (HNO_3 , 69%, Wako Pure Chemical Industries, Ltd.), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 95%, Wako Pure Chemical Industries, Ltd.), acetone ($\text{C}_3\text{H}_6\text{O}$, 99%, Nacalai Tesque, Inc.) were all commercial reagents and were used as received.

Pd/PDA-rGO synthesis

A mixture of 180 mL concentrated H_2SO_4 and 20 mL concentrated H_3PO_4 was gradually added into a beaker containing 1.5 g graphite and 9 g KMnO_4 , which was placed in an ice bath to prevent overheating. Then the beaker was placed in a water bath at 323 K under magnetic stir. After 12 hours, the solution was poured into another beaker containing 200 g ice and 1.5 mL H_2O_2 (30%). Then, the solid precipitate (graphene oxide, GO) was obtained by centrifugation, washing with water (100 mL), HCl (30%, 100 mL) and ethanol (100 mL) for two times and drying in vacuum oven at room temperature for over 72 h. Then, 0.5 g dried GO after grinding to powders was dispersed in 500 mL de-

ionized water under sonication. After 2.5 hours, 40 mL acetone containing 2.7 g *p*-phenylenediamine (PDA) was gradually added into the GO dispersed water solution and stirred for 48 hours to prepare the PDA-GO. The resultant PDA-GO was separated by centrifugation, washing with water and acetone, and dried in vacuum oven at room temperature for over 48 h. Then the obtained PDA-GO was dispersed in 250 mL deionized water, and an aqueous solution of K_2PdCl_4 (0.9 mmol) was added into the PDA-GO solution under sonication. After being sonicated for 30 min, 5 mL deionized water solution containing 0.3 g $NaBH_4$ was added and the mixture was stirred for 45 min, resulting the formation of Pd/PDA-rGO catalyst. Finally, the Pd/PDA-rGO catalyst was obtained by centrifugation, washing with deionized water and drying in vacuum oven at room temperature for over 48 hours.

PdAu/PDA-rGO synthesis

The process of synthesizing the PdAu/PDA-rGO was almost the same as the process of synthesizing the Pd/PDA-rGO. The only difference is that the same molar amount of $HAuCl_4 \cdot 4H_2O$ and K_2PdCl_4 were dissolved in deionized water together and co-precipitated simultaneously on the PDA-rGO.

Instrumentation

X-ray diffraction (XRD) patterns of the catalyst before and after reactions were collected by a Rigaku Smartlab X-ray diffractometer (Cu-K α source, 40 kV, 30 mA). SEM and TEM images of the catalyst were obtained with a scanning electron microscopy (SEM, Hitachi S-4800) operating at 15 kV and a transmission electron microscopy (TEM, Tecnai G² 20) operating at 200 kV, respectively. Pd loading of the Pd/PDA-rGO catalyst

was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPS-3100, SII Nano Technology Inc.). A Horiba FT-720 Fourier transform infrared spectrometer (FR/IR) was used to measure the IR spectra of the solid samples. Gas samples after formic acid decomposition reactions were analyzed by a Shimadzu GC-8A gas chromatograph analyzer equipped with one molecular sieve column and one Porapak Q column using argon (Ar) as the carrier gas. Formic acid concentration in the reaction solution was measured by a Shimadzu Nexera X2 HPLC system with a UV detector at 210 nm equipped with an ion exclusion column (KC-811, Showa Denko K.K.) with 10 mmol/L phosphoric acid aqueous solution as an eluent. The BET surface area of the catalyst were measured with a N₂ adsorption/desorption method at liquid nitrogen temperature (77 K) by a Belsorp-mini apparatus (MicrotracBEL Corp., Japan) after dehydration under vacuum at 120 °C for 4 h.

Table S1. BET surface areas of the Pd/PDA-rGO catalyst before and after the FA decomposition reaction.

	S_{BET} (m ² /g)
Before	11
After	20

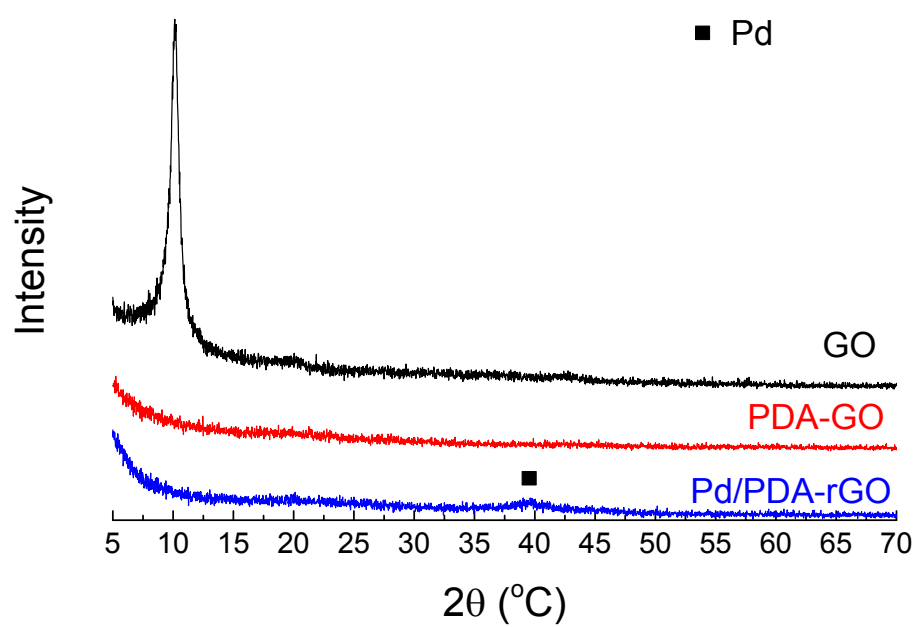


Figure S1. X-ray diffraction spectra of GO, PDA-GO and Pd/PDA-rGO.

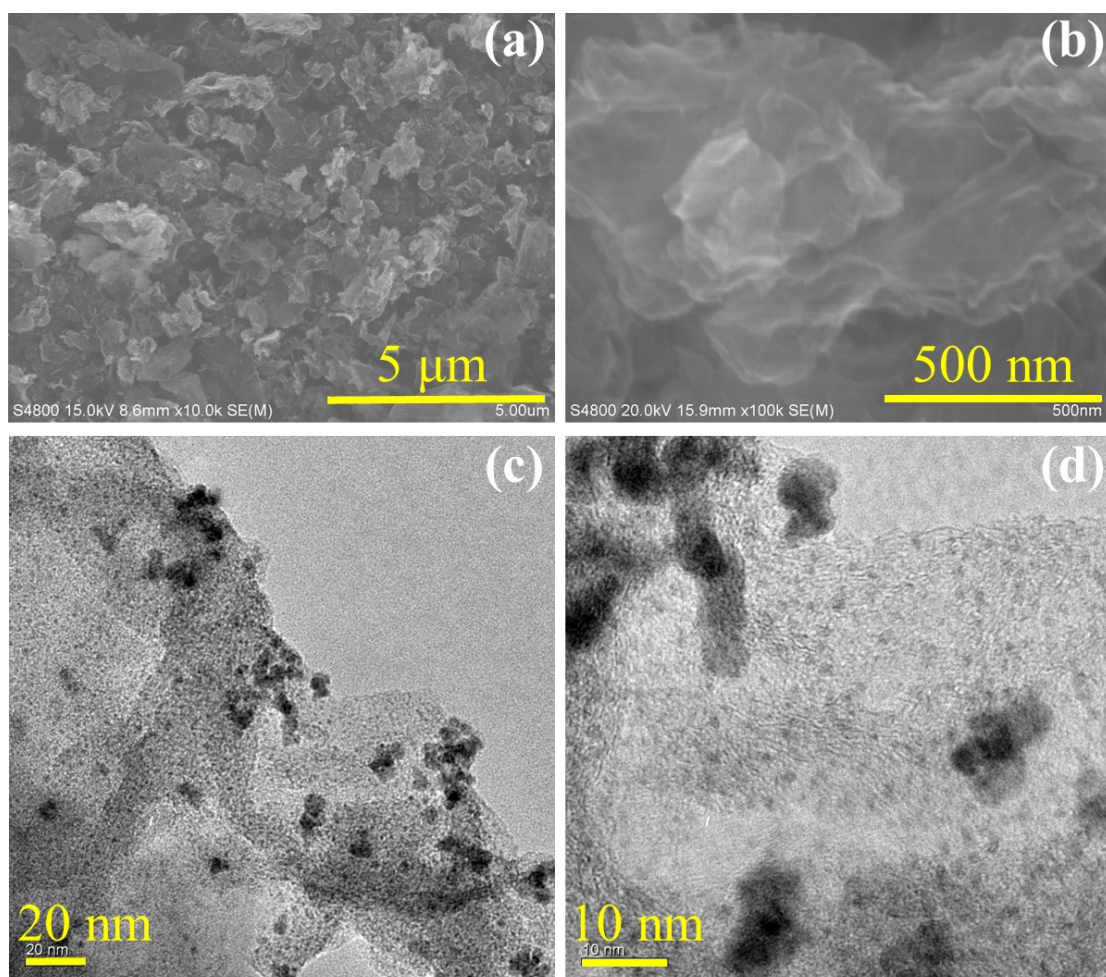


Figure S2. SEM ((a) and (b)) and TEM ((c) and (d)) images of the Pd/PDA-rGO catalyst.

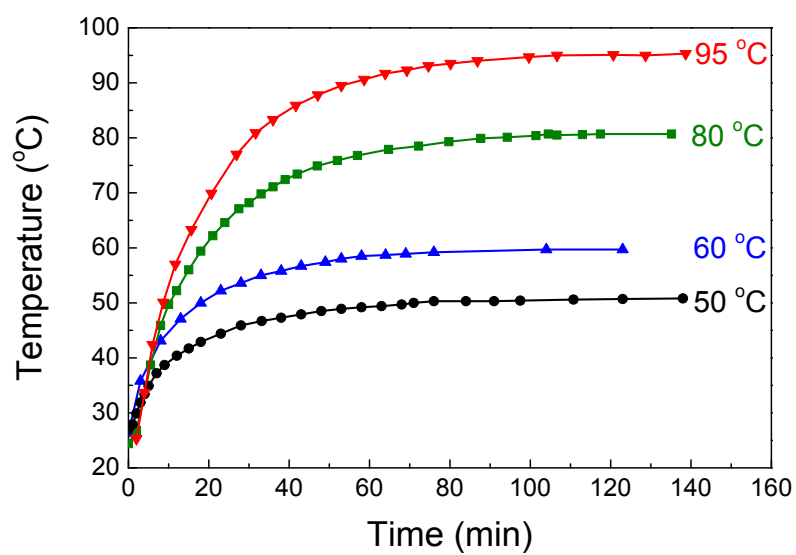


Figure S3. Actual temperature in the tubular reactor as functions of time (tested by using the de-ionized water as the intermediate).

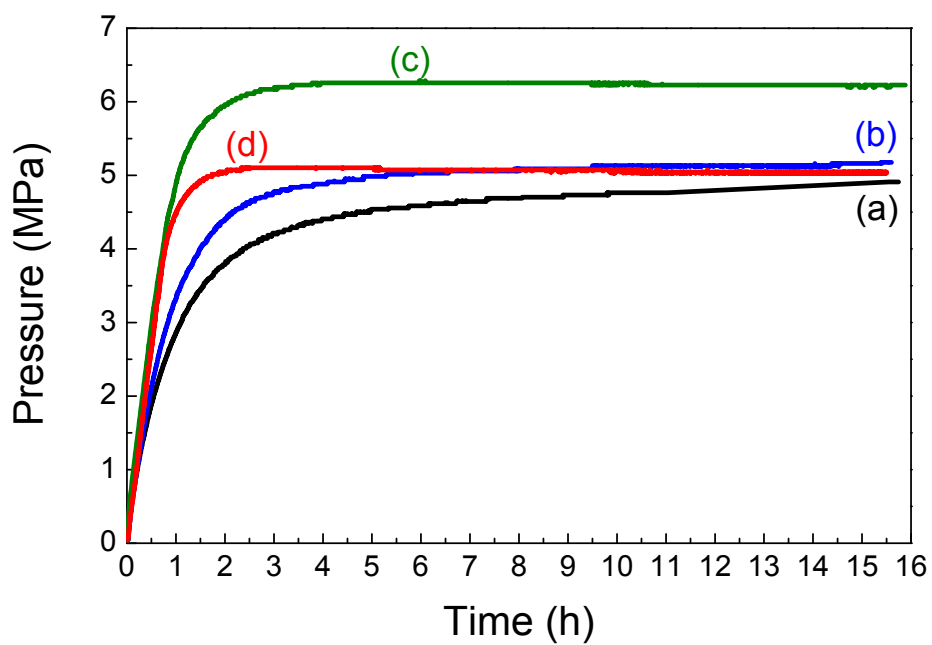


Figure S4. Variation of gas pressure with time at (a) 50, (b) 60, (c) 80, and (d) 95 °C (solution: 6.7 mol/L formic acid + 6.7 mol/L sodium formate; liquid volume: 6 mL; catalyst: 10 mg).

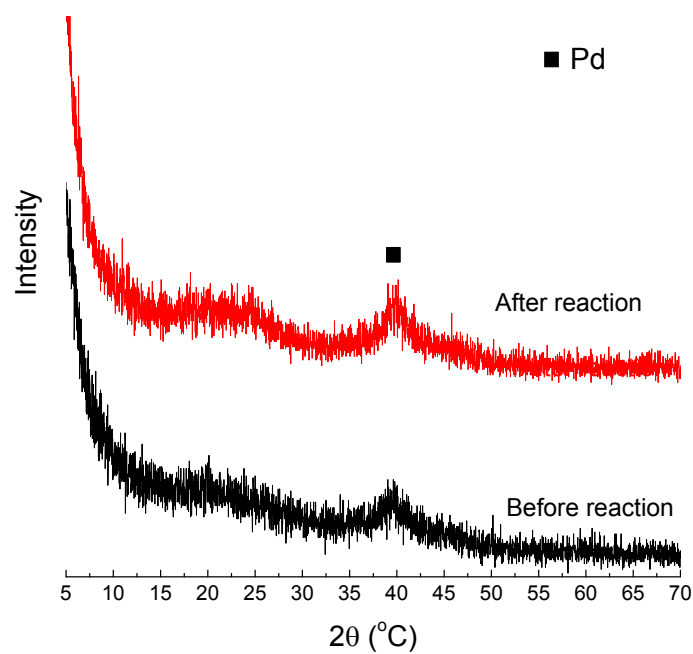


Figure S5. X-ray diffraction spectra of the Pd/PDA-rGO catalyst before and after reaction (solution: 6.7 mol/L formic acid + 6.7 mol/L sodium formate; liquid volume: 6 mL; catalyst: 10 mg; temperature: 80 $^{\circ}\text{C}$; time: 4 h).

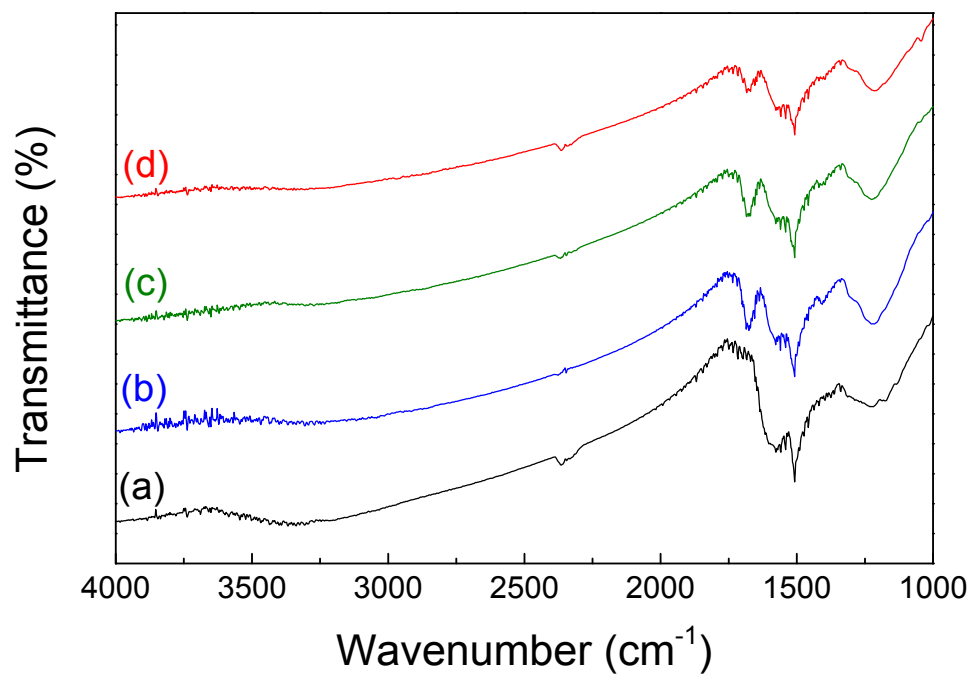


Figure S6. FT-IR spectra of the Pd/PDA-rGO (a) before the reaction and after reactions at (b) 50, (c) 60, and (d) 80 °C, respectively (solution: 6.7 mol/L formic acid + 6.7mol/L sodium formate; liquid volume: 6 mL; time: 15 h).

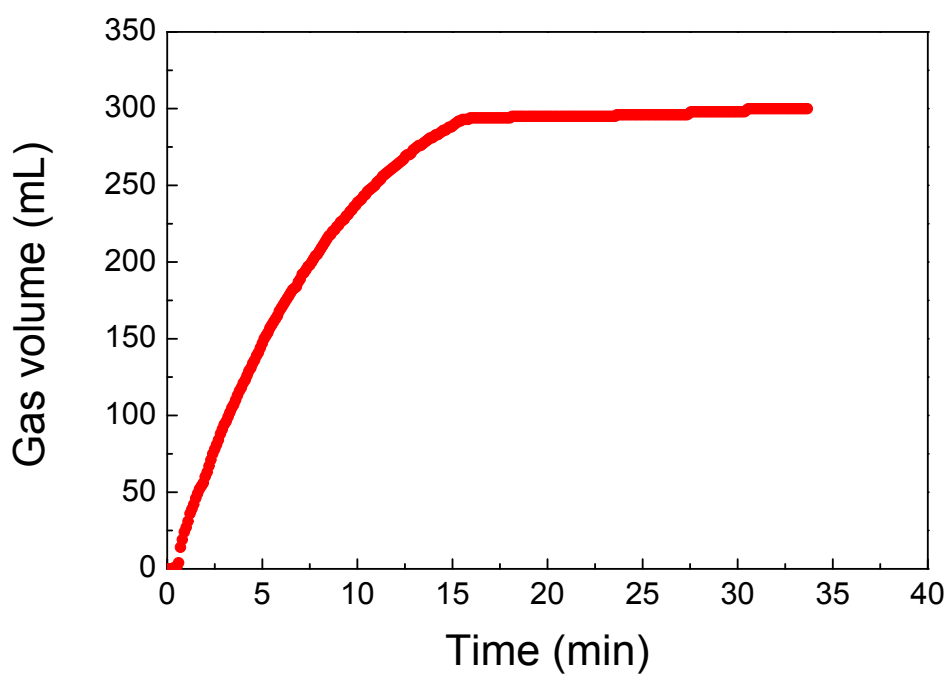


Figure S7. Gas volume as a function of time generated from the decomposition of formic acid at un-pressurized condition (atmospheric pressure) (solution: 2.2mol/L formic acid + 2.2mol/L sodium formate; liquid volume: 3 mL; catalyst: 20 mg; temperature: 80°C).

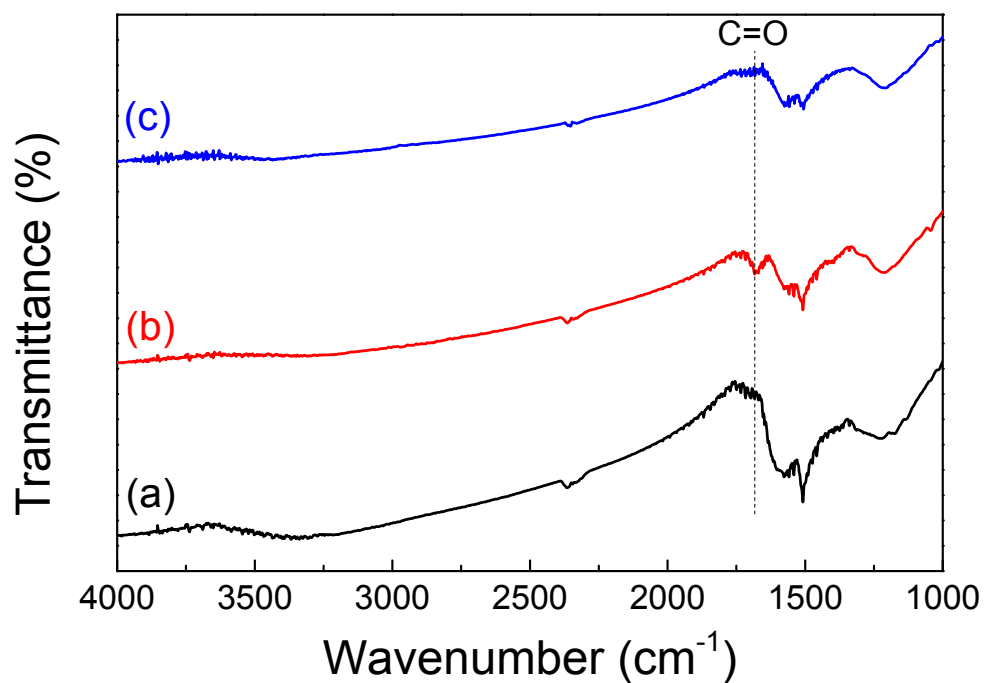


Figure S8. FT-IR spectra of the (a) catalyst before the reaction, (b) catalyst after the reaction, and (c) used catalyst after re-activation in 1 mol/L NaOH solution at 60 °C for 2 h.

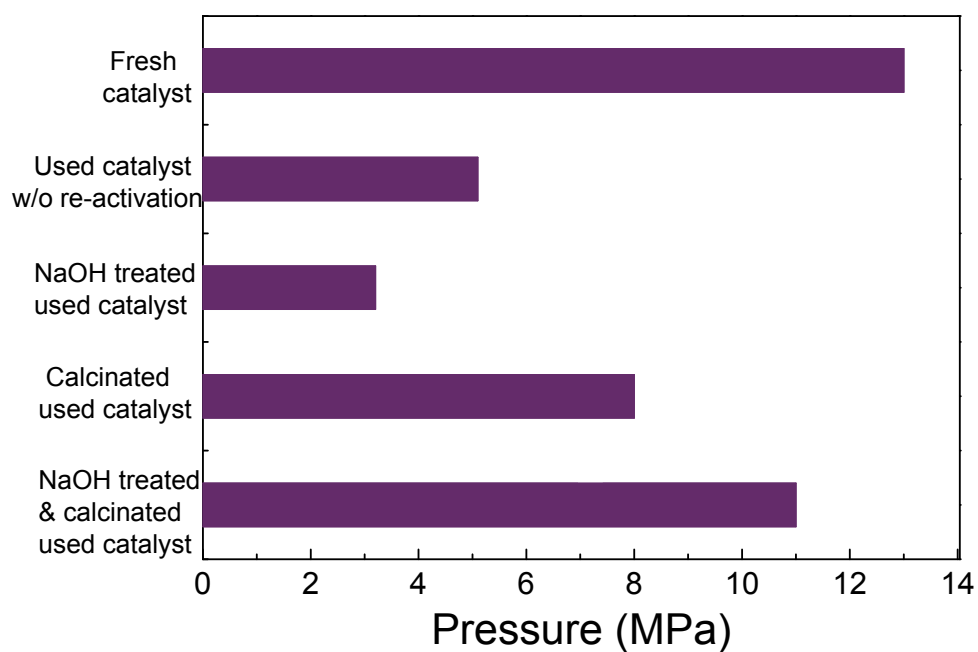


Figure S9. Effect of the catalyst re-activation method on the gas pressure obtained from the formic acid decomposition (reaction conditions: solution, 2 mol/L FA + 2 mol/L SF; liquid, 6 mL; temperature, 80 °C; time, 4 h; catalyst, 20 mg).

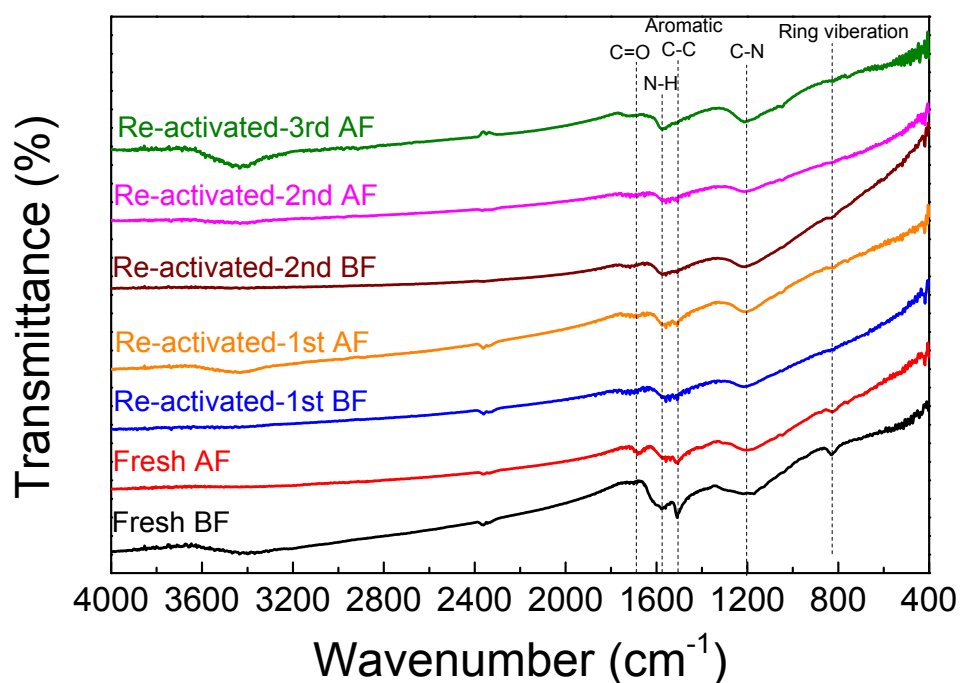


Figure S10. FT-IR spectra of the fresh and cyclically re-activated Pd/PDA-rGO catalyst before and after the FA decomposition reaction (BF: before reaction; AF: after reaction; reaction conditions: solution, 2mol/L formic acid + 2mol/L sodium formate; liquid volume, 6 mL; catalyst, 20 mg; temperature, 80 °C; time, 4 h).

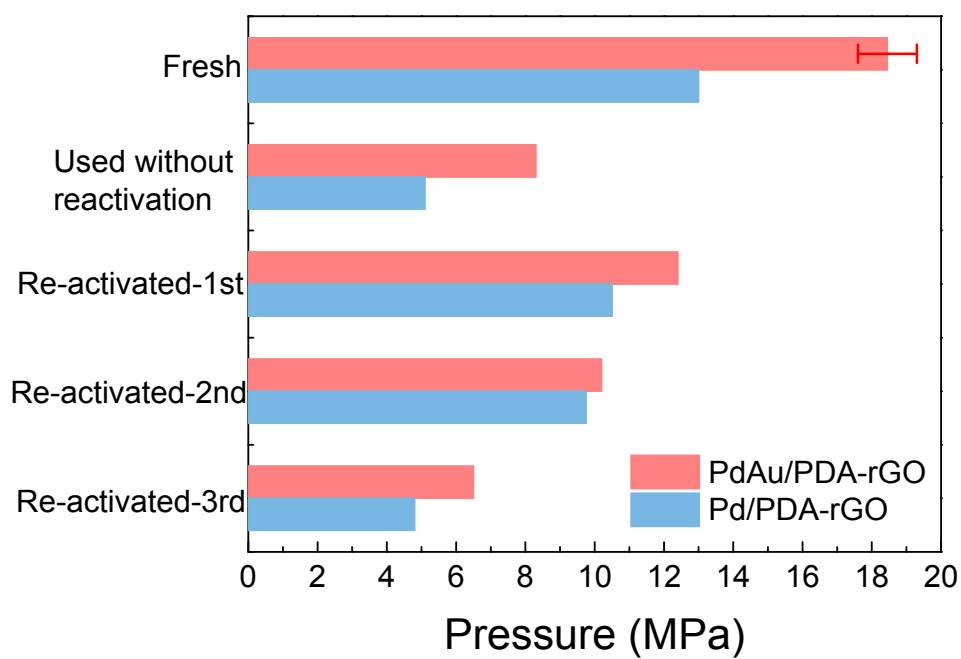


Figure S11. Comparison of the gas pressure obtained with fresh and re-activated Pd/PDA-rGO and PdAu/PDA-rGO catalysts (solution, 2mol/L formic acid + 2mol/L sodium formate; liquid volume, 6 mL; catalyst, 20 mg; temperature, 80 °C; time, 4 h)