

Electronic Supplementary Information

Hydrogenation of CO₂ to Formate Catalyzed by Ru Catalyst Supported on
Copolymerized Porous Organic Polymer

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1. Characterization methods

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a glovebox. All aqueous solutions were degassed before use. The XRD patterns of samples were taken on an XRD-7000S/L diffractometer in the 2θ range of $2^\circ\sim 40^\circ$ at a scanning speed of $5^\circ/\text{min}$ using Al-K α radiation ($\lambda = 1.542$ nm) at ambient temperature. The EA was detected using Vario EL cube instrument. A Renishaw inVia Raman spectrometer equipped with a He-Ne laser excitation source operating at 633 nm, was used for the collection of Raman spectra. The sample was pressed into a KBr-diluted self-supported wafer and placed into the sample holder. The spectrum region was recorded from 400 to 4000 cm^{-1} by averaging 32 scans with a resolution of 4 cm^{-1} . Nitrogen adsorption-desorption isotherms were carried out at 77 K on a JW-BK300 Analyzer instrument. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Before the measurements, the samples were degassed at $200\text{ }^\circ\text{C}$ under a vacuum for 2 h to remove physically adsorbed impurities. TGA was conducted on a thermal analysis system (TGA-1150, Shanghai Jiubin Instrument Co. Ltd.) under a flow of air with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ from 25 to $1000\text{ }^\circ\text{C}$. SEM images were analyzed by using a Nova Nano SEM 450 system electron microscope. All samples were treated with gold coating before the test. XPS spectra were detected on an ESCALAB™ 250Xi system with Al K α radiation as the excitation source. The software XPEPEAK was employed to fit the peaks. The actual ruthenium loading of the samples was confirmed by ICP-OES (Agilent 5110, United States of America). FTIR spectra of the samples were recorded in the range of $45\sim 4000\text{ cm}^{-1}$ on a Nicolet in10 MX & iS10 spectrophotometer. Shimadzu LC-16 liquid chromatography: It can determine the concentration of formic acid/formate in the reaction solution and is used to analyze the TON of the CO_2 hydrogenation reaction. The mobile phase is 0.1% aqueous phosphoric acid solution, and the column is a TSKgel SCX-type column. The flow rate was $0.8\text{ mL}/\text{min}$; column temperature: 40°C ; injection volume: $20\text{ }\mu\text{L}$; run time: 10 min. TEM, STEM, and EDS measurements made use of a Tecnai G2F30 STWIN operating at an accelerating voltage of 200 kV. ^1H NMR spectra were recorded on an AV III 500 HD 500 MHz spectrometer.

2. Synthesis of Porous Organic Polymers and Ru Catalysts

2.1 Synthesis of POP-1 and Ru@POP-1(Cat-1)

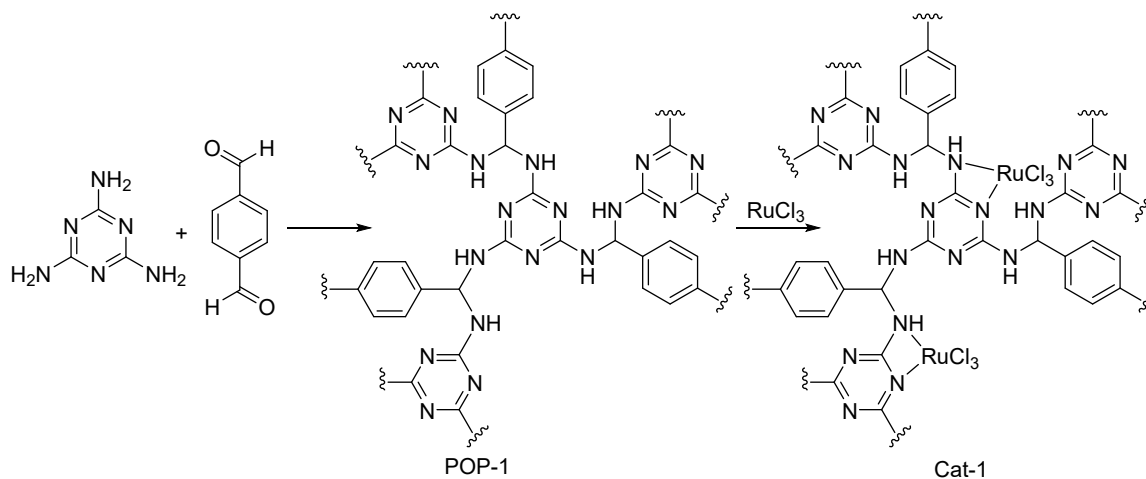


Fig. S1 Synthesis of **POP-1** and **Cat-1**

Melamine (188 mg, 1.5 mmol) and 1, 4-Phthalaldehyde (PTA, 300 mg, 2.25 mmol) were dissolved in DMSO (9.6 mL) in a 25 mL Schlenk tube under argon protection. The reaction was carried out at 180°C for 22 h with continuous stirring at 500 rpm. After stopping the reaction, the contents were allowed to cool naturally. Argon was stopped and the product was isolated by filtration and washed successively with excess acetone, THF, and dichloromethane. The sample was dried under vacuum at 120 °C overnight to obtain the final product **POP-1**. 40 mg **POP-1** was dispersed in methanol (4 mL) by sonication. Then, 2 mg of RuCl₃ was added to the above suspension and further sonicated for 10 min. After sonication, the mixture was stirred at room temperature for 24 h. The solids were filtered, washed with excess acetone and dried under vacuum at 120°C overnight to obtain catalysts **Cat-1**.

2.2 Synthesis of POP-2 and Ru@POP-2(Cat-2)

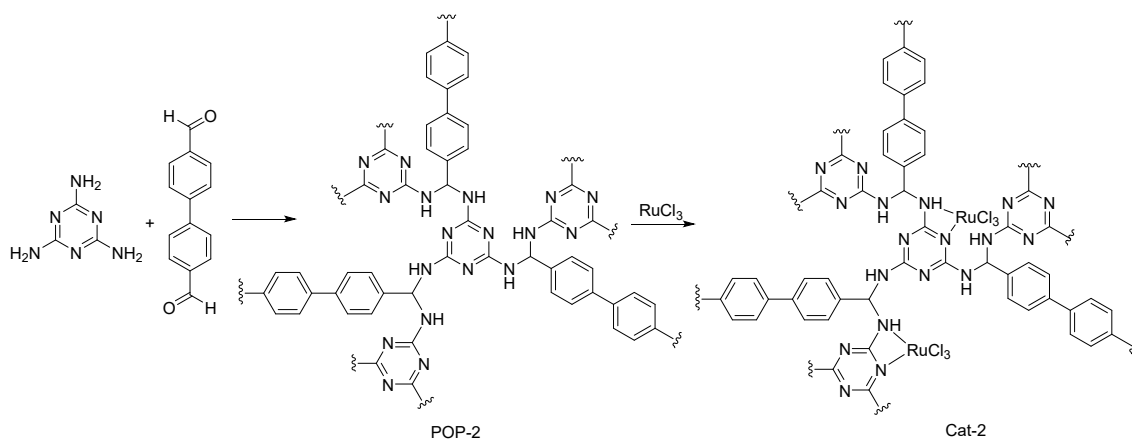


Fig. S2 Synthesis of **POP-2** and **Cat-2**

Melamine (188 mg, 1.5 mmol) and 4,4'-Biphenyldicarboxaldehyde (BPDA 472.8 mg, 2.25 mmol) were dissolved in DMSO (9.6 mL) in a 25 mL Schlenk tube under argon protection. The reaction was carried out at 180°C for 22 h with continuous stirring at 500 rpm. After stopping the reaction, the contents were allowed to cool naturally. Argon was stopped and the product was isolated by filtration and washed successively with excess acetone, THF, and dichloromethane. The sample was dried under vacuum at 120°C overnight to obtain the final product **POP-2**. 40 mg **POP-2** was dispersed in methanol (4 mL) by sonication. Then, 2 mg of RuCl₃ was added to the above suspension and further sonicated for 10 min. After sonication, the mixture was stirred at room temperature for 24 h. The solids were filtered, washed with excess acetone and dried under vacuum at 120 °C overnight to obtain catalysts **Cat-2**.

2.3 Synthesis of POP-3 and Ru@POP-3(Cat-3)

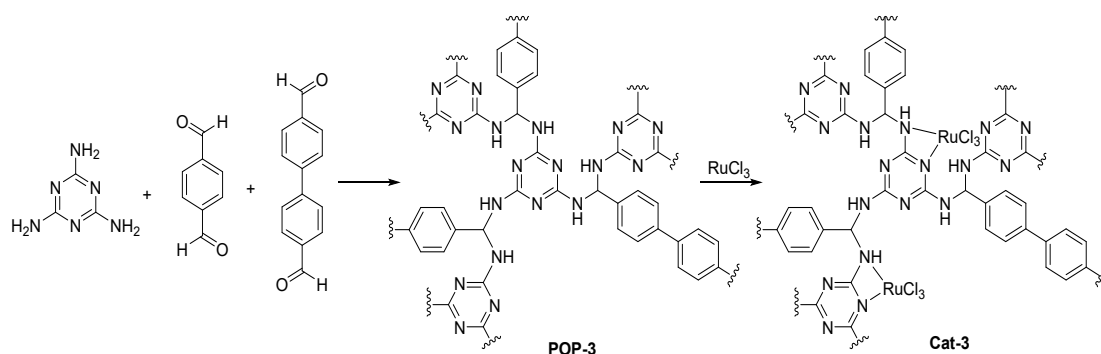


Fig. S3 Synthesis of **POP-3** and **Cat-3**

Melamine (188 mg, 1.5 mmol), PTA (225 mg, 1.69 mmol) and BPDA (118.2 mg, 0.56 mmol) (molar ratio 3:1) were dissolved in DMSO (9.6 mL) in a 25 mL Schlenk tube and protected by argon. The reaction temperature was 180 °C and the reaction time was 22 h with continuous stirring at 500 rpm. After stopping the reaction, the contents were allowed to cool naturally. Argon was stopped and the product was isolated by filtration, after which it was washed with excess acetone, THF and dichloromethane, respectively. The sample was dried under vacuum at 120 °C overnight to obtain the final product **POP-3**. 40 mg **POP-3** was dispersed in methanol (4 mL) by sonication. Then, 1/2/4 mg of RuCl₃ was added to the above suspension and further sonicated for 10 min. After sonication, the mixture was stirred at room temperature for 24 h. The solids were filtered, washed with excess acetone and dried under vacuum at 120 °C overnight to obtain catalysts **Cat-3**.

3. Catalytic reaction

All hydrogenation reactions were performed in a 25 mL capacity customized stainless steel reactor equipped with temperature and pressure sensors as well as gas inlet and outlet ports. In a typical hydrogenation experiment, the catalyst (5 mg) was loaded into the kettle along with an aqueous solution of base (5 mL) and shut down. Before the start of the reaction, the reactor was purged with Ar gas to remove any residual air and then filled with a mixture of CO₂ and H₂ in a 1:1 ratio to achieve the desired reaction pressure at room temperature. The reactor was heated to the specified temperature while continuously magnetic stirring at 1000 rpm. After the reaction, the mixture was allowed to cool naturally and the remaining gas was slowly released through a release valve. A liquid sample was collected from the reactor and filtered using a 0.2 μm filter. Finally, the formate concentration was measured using HPLC equipment. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to accurately determine the ruthenium metal content in the synthesized catalysts.

Table S1 Results of **Cat-1** catalyzed hydrogenation of CO₂ to formate at different reaction times

Entry	T (h)	Conc. _{formate} (M)	TON
1	0.25	0.017	212
2	0.5	0.046	574
3	1	0.072	898
4	2	0.16	1996
5	4	0.19	2371
6	8	0.26	3244
7	12	0.32	3993
8	24	0.39	4866

Note: Reaction conditions: catalyst dosage of 5 mg, 5 mL of water, reaction temperature of 120 °C, reaction pressure of 3 MPa, 1 M triethylamine, 0.81 wt% Ru.

Table S2 Results of **Cat-2** catalyzed hydrogenation of CO₂ to formate at different reaction times

Entry	T (h)	Conc. _{formate} (M)	TON
1	0.25	0.030	399
2	0.5	0.063	838
3	1	0.090	1197
4	2	0.17	2261
5	4	0.22	2926
6	8	0.29	3857
7	12	0.34	4522
8	24	0.46	6117

Note: Reaction conditions: catalyst dosage of 5 mg, 5 mL of water, reaction temperature of 120 °C, reaction pressure of 3 MPa, 1 M triethylamine, 0.76 wt% Ru.

Table S3 Results of **Cat-3** catalyzed hydrogenation of CO₂ to formate at different reaction times

Entry	T (h)	Conc. _{formate} (M)	TON
1	0.25	0.044	601
2	0.5	0.062	847
3	1	0.096	1311
4	2	0.18	2458
5	4	0.25	3415
6	8	0.34	4685
7	12	0.41	5600
8	24	0.53	7239

Note: Reaction conditions: catalyst dosage of 5 mg, 5 mL of water, reaction temperature of 120 °C, reaction pressure of 3 MPa, 1 M triethylamine, 0.74 wt% Ru.

4. The elemental composition of porous organic polymers supports

Table S4 Elemental composition of porous organic polymers supports

sample	N(%)	C(%)	H(%)	C/N ratio	C/H ratio
POP-1	41.58	39.47	4.78	0.9491	8.2959
POP-2	36.44	35.91	5.22	0.9855	6.8834
POP-3	36.27	36.49	5.01	1.0061	7.2855

5. BJH pore size distributions

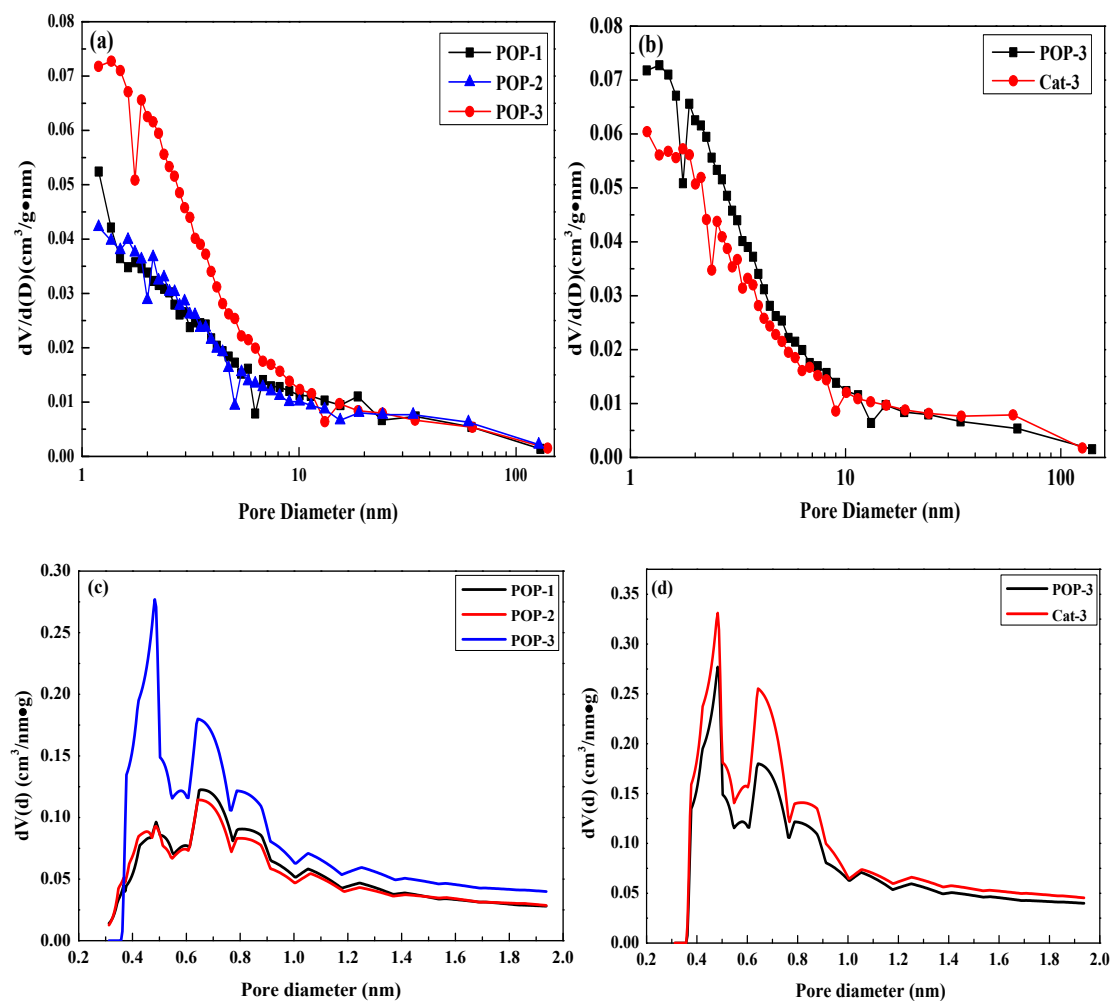


Fig S4. (a) BJH pore size distribution of **POP-1**, **POP-2** and **POP-3**;

(b) BJH pore size distributions of **POP-3** and **Cat-3** catalyst;

(c) HK pore size distribution of **POP-1**, **POP-2** and **POP-3**;

(d) HK pore size distributions of **POP-3** and **Cat-3** catalyst.

6. ^1H NMR spectra of the reaction solution

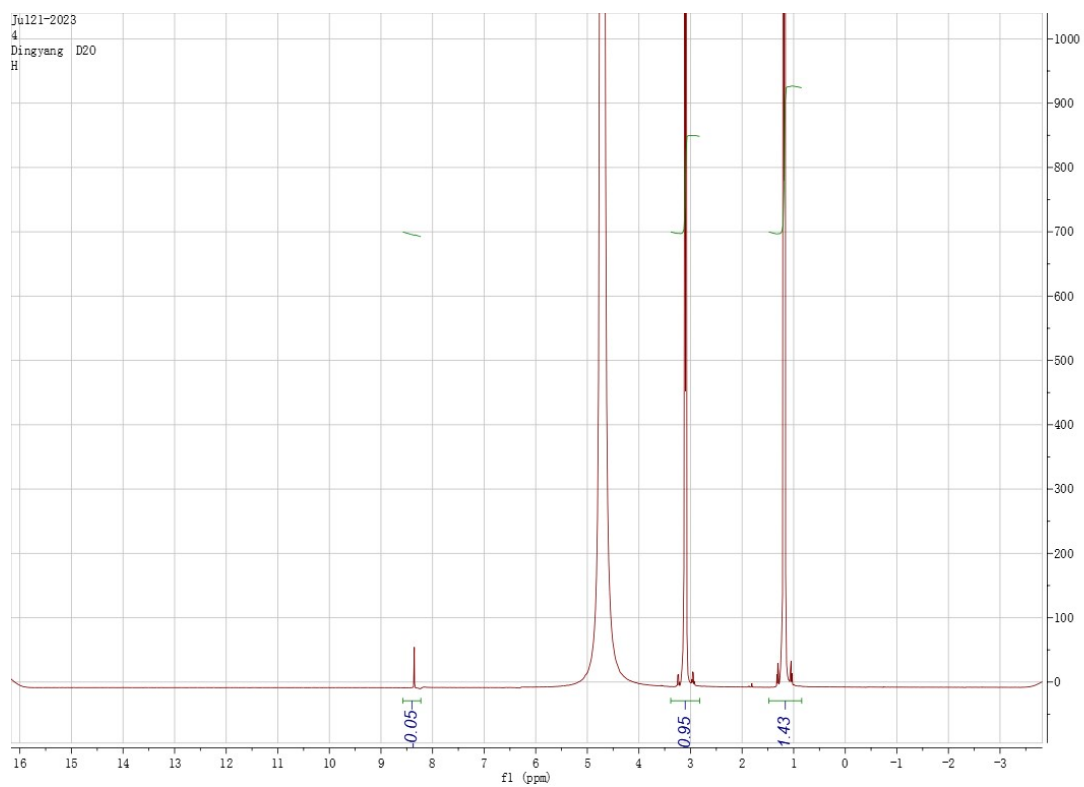


Fig S5. ^1H NMR spectra of the solution obtained in Table S2 entry 1 (D_2O).

7. The results of gas chromatography

Table S5 The GC results of the gas mixture obtained from Table S2 entry 4.

t (min)	Gas
1.112	air
9.085	CO ₂

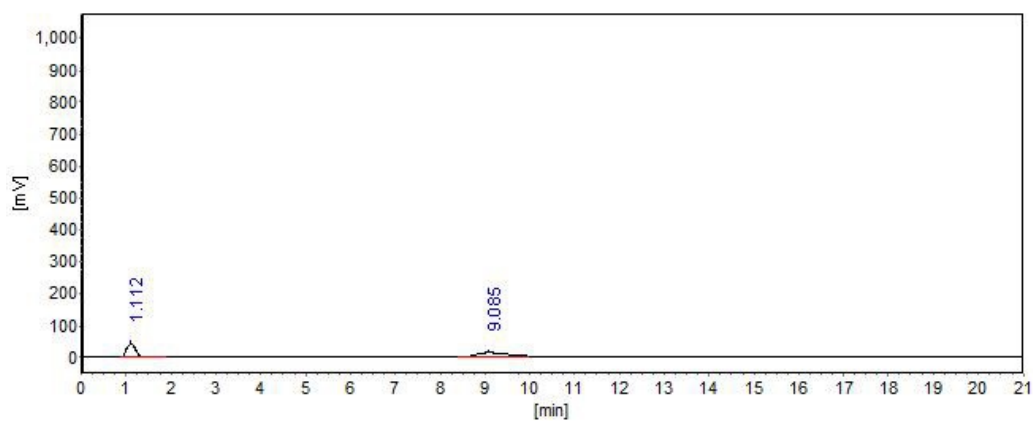


Fig. S6 The GC results of the gas mixture obtained from Table S2 entry 4.

8. Heterogeneity test results of Cat-3

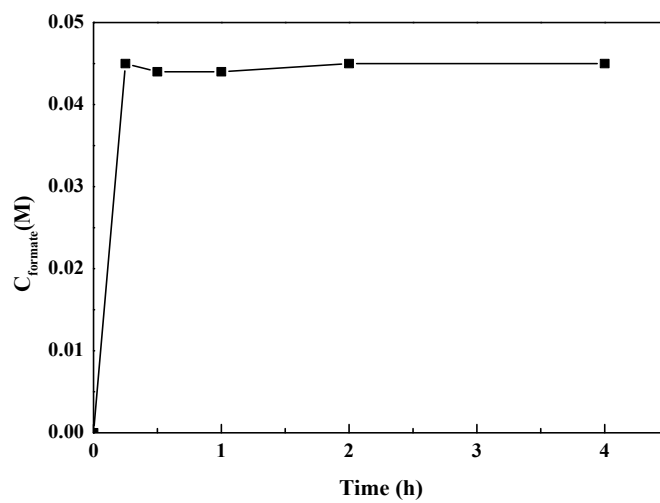


Fig S7. Heterogeneity test results of **Cat-3**

9. Activity comparison of POP-supported Ru catalysts

Table S6 Activity comparison of POP-supported Ru catalysts

Entry	Catalyst	Time (h)	Temperature (°C)	Pressure of CO ₂ /H ₂ (bar)	TON	ref
1	Ir-PN/SBA-15	2	60	40	2800	[1]
2	bpy-CTF-[IrCp*Cl]Cl	2	120	80	5000	[2]
3	[bpy-CTF-Ru(acac) ₂]Cl	2	120	80	6980	[3]
4	Ir _{4.7} @bpy-CTF-400	2	120	80	5000	[4]
5	Ru@pDPPE	4	120	100	13170	[5]
6	IrCl ₃ -phen-POP	2	140	80	14330	[6]
7	Ru ³⁺ POPs@MHCS	24	120	40	1200	[7]
8	Ru/N-MCHS-900	2	120	80	7550	[8]
9	Ru/KAPs-Ph-PPh ₃	12	120	60	1470000	[9]
10	RuCl ₃ @PY-CTF	2	120	80	2067	[10]
11	bpy-PP-POP	24	140	5.6	20041	[11]
12	Cat -3	2	120	30	2458	This work
13	Cat -3	24	120	30	7239	This work

10. References

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