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Supporting Information

Cobalt Single-Atom Catalysts with High Stability for Selective Dehydrogenation of Formic Acid

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Supporting Information

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1. General Experimental Details

Dehydrogenation reactions were performed under Ar with exclusion of air using standard Schlenk techniques. Formic acid (FA) was purified by reflux and distilled following standard procedures and then stored under argon atmosphere. Water was degassed by bubbling argon for 8 hours. Solvents were used directly without purification. HCO_2Na and $LiBF_4$ were used and stored as received. The metal precursors $Co(NO)_3•6H_2O$, $Zn(NO)_3•6H_2O$ and KOH were obtained from Alfa Aesar, 2-methylimidazole were obtained from Arcos Organics chemicals, all these reagents were used directly without further purification.

The power X-ray diffraction (PXRD) pattern was carried out on a Stoe STADI P diffractometer, equipped with a linear Position Sensitive Detector (PSD) by Cu Kα radiation (λ = 1.5406 Å). The software WinXpow (Stoe) was used for processing. The patterns were assigned according to the Powder Diffraction File (PDF) database of the International Centre of Diffraction Data (ICDD).

EPR (electron paramagnetic resonance) spectra were recorded on an X-band Bruker EMX CW-micro EPR spectrometer equipped with an ER4119HS high-sensitivity resonator using a microwave power of Ca 6.9 mW, modulation frequency of 100 kHz and modulation amplitude up to 5 G. For low temperature measurements, the EPR spectrometer was equipped with a temperature controller and liquid N_2 cryostat. For Ph_3P ligand involved test, EPR spectrum of Co-SACs (6 mg) was firstly measured at 100 K then excess amount of Ph_3P (10 mg) was added to the EPR tube, heated to 90 ^oC (just above the meting point of Ph_3P (80 ^oC), and measured again the EPR spectrum at 100 K.

TEM (Transmission Electron Microscopy) measurements were performed on a Thermo Fisher Titan Themis, 60-300 “cubed” microscope fitted with an aberration-correctors for the imaging and the probe forming lens at 300 kV. The microscope was also equipped with an energy-dispersive x-ray-spectrometer (EDXS) for chemical analysis. For pretreatment, powder was dispersed in isopropyl alcohol and sonicated for about 10 minutes. Then a 20 μL of the dispersed solution was dropped over 300 mesh Cu grid and dried at room temperature for TEM analysis

The X-ray absorption spectra were collected on the beamline BL01C1 in NSRRC. The radiation was monochromatized by a Si (111) double-crystal monochromator. XANES and EXAFS data reduction and analysis were processed by Athena software. The obtained XAFS data was processed in Athena

(version 0.9.25) for background, pre-edge line and post-edge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.25). The k^2 weighting, k-range of 3 - 12 $Å^{-1}$ and R range of 1 - ~3 Å were used for the fitting. The model of bulk Co, CoPc and Co_3O_4 were used to calculate the simulated scattering paths. The four parameters, coordination number, bond length, Debye-Waller factor and E_0 shift (CN, R, σ^2, ΔE_0) were fitted without anyone was fixed, constrained, or correlated. For Wavelet Transform analysis, the $\chi(k)$ exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 1 - 4 Å, k range, 0 - 13 $Å^{-1}$; k weight, 2; and Morlet function with κ=10, σ=1 was used as the mother wavelet to provide the overall distribution.

The XPS (X-ray Photoelectron Spectroscopy) measurements were recorded with a VG ESCALAB220iXL with monochromated AlKα radiation (E = 1486.6 eV). All curves were deconvoluted with Gaussian-Lorentzian curves for quantitative analysis. Meantime, the peak areas were divided by a sensitivity factor from the element specific Scofield factor and the transmission function of the spectrometer.

N_2 adsorption isothermal curves were tested by the instrument of ASAP 2020 from Micromeritics (USA). Measurements were done with standard BET procedure:

a): pretreatment of the sample up to 400 °C at 0.01 mbar to desorb gases and water

b): adsorption and desorption of N_2 at -196 K with a low pressure from 3×10^{-6} (P/P_0)

c): calculations: BET-plot, t-plot and pore size distribution via DFT (model: slit pores for carbon)

Gas content was determined by gas-phase GC (6890A, Agilent Technologies). The gas was analyzed by two detection systems:

GC a): HP Plot Q / FID – hydrocarbons, Carboxen / TCD - permanent gases, He carrier gas.

GC b): Carboxen / TCD / Methanizer / FID - permanent gases, He carrier gas.

The H_2, CO_2, CO, and CH_4 amounts were determined and their ratios established.

2. Calculation of gas production rate

The gas production rate was calculated by equation **(S1)**:

$$\text{Gas production rate} = \frac{V_{gas}}{m_{cat} \times t} \qquad (\boldsymbol{S1})$$

where V_{gas} is the gas volume corrected by blank volume, and m_{cat} is the weight of catalyst, respectively.

The turnover frequency (TOF) was calculated by equation **(S2):**

$$TOF = \frac{\frac{V_{gas}}{(V_{m,H_2,25°C} + V_{m,CO_2,25°C})}}{n_{cat} \times t} \qquad (\boldsymbol{S2})$$

The calculation of $V_{m,H_2,25°C}$ and $V_{m,CO_2,25°C}$ were carried out using equation (**S3**) and (**S4**):

$$V_{m,H_2,25°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.48\ \frac{L}{mol} \qquad (\boldsymbol{S3})$$

$$V_{m,CO_2,25°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.36\ \frac{L}{mol} \qquad (\boldsymbol{S4})$$

Where:

R: 8.3145 $m^3 \cdot Pa \cdot mol^{-1} \cdot K^{-1}$;

T: 298.15 K;

P: 101325 Pa;

a (H_2): $24.7 \cdot 10^{-3} \cdot Pa \cdot m^6 \cdot mol^{-2}$ and a (CO_2): $36.5 \cdot 10^{-2} \cdot Pa \cdot m^6 \cdot mol^{-2}$;

b (H_2): $26.6 \cdot 10^{-6}\ m^3 \cdot mol^{-1}$ and b (CO_2): $42.7 \cdot 10^{-6}\ m^3 \cdot mol^{-1}$

3. Preparation of Co-N-C Heterogeneous Catalyst

3.1 Synthesis of ZnCo-BMOF

The synthesis method was referenced by Wang et al. Typically, $Co(NO_3)_2 \cdot 6H_2O$ (0.546 g) and $Zn(NO_3)_2 \cdot 6H_2O$ (1.116 g) were mixed and dissolved in 30 mL of methanol as solution 1. Then, 2-methylimidazole (1.232 g) was dropped into a 30 mL of methanol as solution 2. The solution 1 was subsequently added to solution 2 under vigorously stirring for 6 hours at room temperature. As-obtained precipitates were collected by centrifugation at 5000 rpm for 20 minutes, washed five times with methanol, and finally dried overnight.

3.2 Synthesis of Co-ZIF-67

The procedure was same as the synthesis of ZnCo-BMOF except for $Zn(NO_3)_2 \cdot 6H_2O$ introduction. Typically, $Co(NO_3)_2 \cdot 6H_2O$ (0.546 g) was dissolved in 30 mL of methanol as solution 1. Then, 2-methylimidazole (1.232 g) was dropped into 30 mL of methanol as solution 2. The solution 1 was subsequently added to solution 2 under vigorously stirring for 6 hours at room temperature. As-obtained precipitates were collected by centrifugation at 5000 rpm for 20 minutes, washed five times with methanol, and finally dried overnight.

3.3 Synthesis of Zn-ZIF-8

The procedure was the same as ZnCo-BMOF synthesis except for $Co(NO_3)_2 \cdot 6H_2O$ introduction. Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (1.116 g) was dissolved in 30 mL of methanol as solution 1. Then, 2-methylimidazole (1.232 g) was dropped into a 30 mL of methanol as solution 2. The solution 1 was subsequently added to solution 2 under vigorously stirring for 6 hours at room temperature. As-obtained precipitates were collected by centrifugation at 5000 rpm for 20 minutes, washed five times with methanol, and finally dried overnight.

3.4 Synthesis of Co-N-C(SACs) catalyst

The dried powder of ZnCo-BMOF was calcinated with a heating rate of 10 °C min^{-1} kept at 800 °C for 1 hour, 900 °C for 1 hour and 1000 °C for 1 hour under argon flow in a tube furnace. Then it naturally cooled to room temperature. As-prepared samples were directly used without acid etching and other post-treatment. Notably, the catalysts which labelled with Co-SACs-X, meaning X was the final calcination temperature. For Co-SACs-800 and Co-SACs-900, the final temperatures were kept at 800 °C and 900 °C for 3 hours, respectively.

3.5 Synthesis of Co-N-C(NPs) catalyst

The dried powder of Co-ZIF-67 was calcinated with a heating rate of 10 °C min^{-1} kept at 800 °C for 1 hour, 900 °C for 1 hour and 1000 °C for 1 hour under argon flow in a tube furnace. Then it naturally cooled to room temperature. As-prepared samples were directly used without acid etching and other post-treatment. Notably, the catalysts which labelled with Co-NPs-X, meaning X was the final calcination temperature. For Co-NPs-800 and Co-NPs-900, the final temperatures were kept at 800 °C and 900 °C for 3 hours, respectively.

3.6 Synthesis of Co(1)/phen(7)/C catalyst

The synthesis method was same like provided in our previous report. Typically, $Co(OAc)_2 \cdot 4H_2O$ (126.8 mg, 0.5 mmol) and 1,10-phenanthroline (3.5mmol) (Co:phenanthroline = 1:7 molar ratio) were stirred in ethanol (20 mL) for 30 minutes at room temperature. Then Vulcan XC72R carbon (696 mg) was added and the mixture was stirred at 60 °C for 4 hours with refluxing. The ethanol was removed by a rotary evaporator and dried overnight. The black powder was grinded and transferred into a ceramic crucible for calcination in the oven. The oven was heated to 800 °C at a rate of 25 °C per min and held at 800 °C for 2 h under argon, then cooled to room temperature.

4. Comparison of Heterogeneous Catalysts for the Dehydrogenation of FA

Table S1. Heterogeneous catalysts for the dehydrogenation of FA.

Catalyst	Other reactants	Temp. [°C]	TOF [h^{-1}]	Ref.
Mono-metallic system				
Pd/C	citric acid/ Sodium formate	25	64	[1]
Pd/N-C_M (≈2.6 nm)	No	100	436	[2]
Pd/NH_2-MIL-125	Sodium formate	32	214	[3]
Au clusters/Al_2O_3	Triethylamine	25	64	[4]
Au clusters/ZrO_2	Triethylamine	25	252	[5]
Pd/C_m	Sodium formate	60	7256	[6]
Pd@CN900K	Sodium formate	60	14400	[7]
Bimetallic system				
AgPd alloy NPs (≈4 nm)	No	50	230	[8]
AgPd alloy NPs (≈2.2 nm)	No	50	382	[9]
AgPd/MIL-101	Sodium formate	80	848	[10]
PdAu/C-CeO_2	Sodium formate	92	227	[11]
$Ag_{18}Pd_{82}$@ZIF-8	Sodium formate	80	580	[12]
AuPd/NH_2-N-rGO (≈2.2 nm)	Sodium formate	40	7953	[13]
Trimetallic system				
$Pd_{0.58}Ni_{0.18}Ag_{0.24}$/C(≈5.6 nm)	Sodium formate	50	85	[14]
$Au_{0.28}Pd_{0.47}Co_{0.25}$/ MIL-101–$NH_2$	No	25	347	[15]
PdAuEu/C	Sodium formate	92	387	[16]
$Co_{0.30}Au_{0.35}Pd_{0.35}$/C	No	25	80[a]	[17]
CoAuPd/DNA-rGO	No	25	85[a]	[18]
$Ni_{0.40}Au_{0.15}Pd_{0.45}$/C	No	25	12[a]	[19]
Only non-noble metal				
Co(1)/phen(7)/C	No	98	220[a]	[20]
Co-N-C (SACs)	No	98	357[a]	This work

[a]Initial TOF values calculated for the initial stages of the catalytic reactions.

5. Procedure for the Dehydrogenation of FA

5.1 Burette measurements

As shown in figure S1, the setup of activity measurements was done by a 3-neck double wall reactor attached to a condenser and manual burettes.

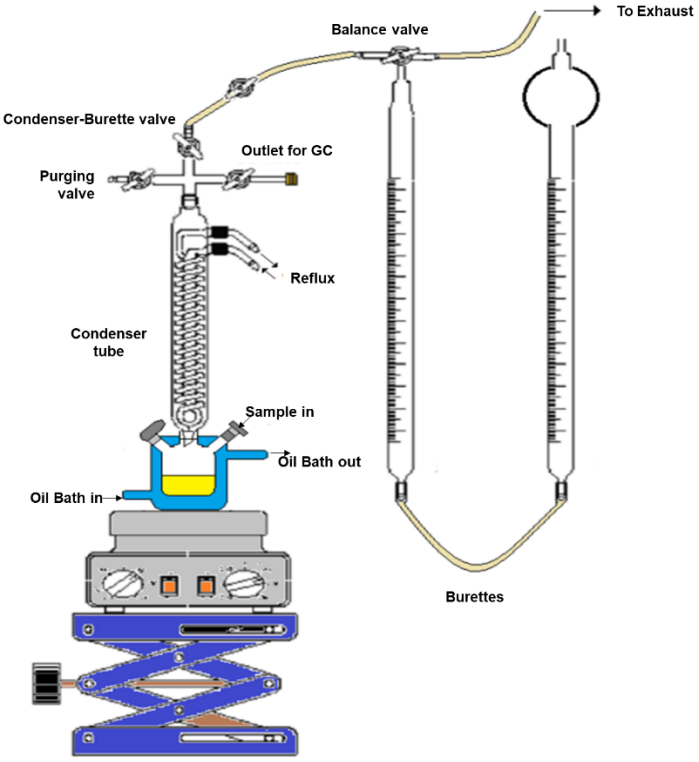


Figure S1. Manual burette setup.

5.2 Procedure for the dehydrogenation of FA

The reaction vessel was evacuated and flushed with argon 6 times. FA (10 mmol, 377 µL) and solvent were added under an argon flow. The vessel was heated to the desired temperature with the help of thermostate and let equilibrate for 20 min. Then, the catalyst (30 mg) was dropped into the reaction vessel under argon flow with a mini-Teflon cup. Then the setup was vented to the open air to release the pressure in the burette, closed again, followed by starting measurement of the evolved gas volume using a manual burette. After finishing the reaction during the desired time, the degassed syringe was used to obtain a gas sample analyzed by gas chromatography.

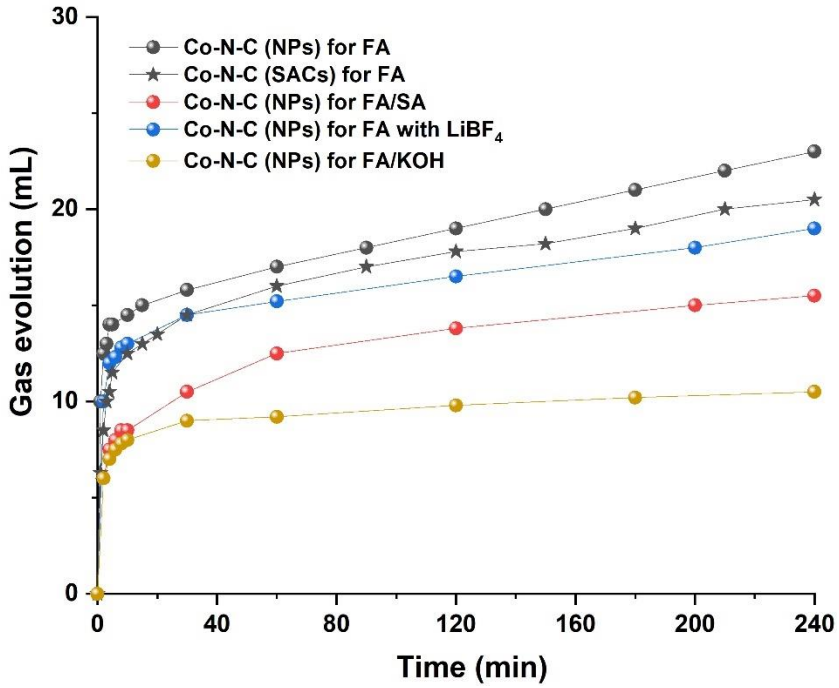


Figure S2. Investigation of pH and additive effect on the Co-N-C catalysts. Reaction conditions: FA (10 mmol) or FA (1.35 mmol) with SA (8.65 mmol) for pH of 7 or FA (10 mmol) with KOH (15 mmol) for pH of 14, catalyst (30 mg) in water (6 mL) . Furthermore, $LiBF_4$ doping with 1mmol when used.

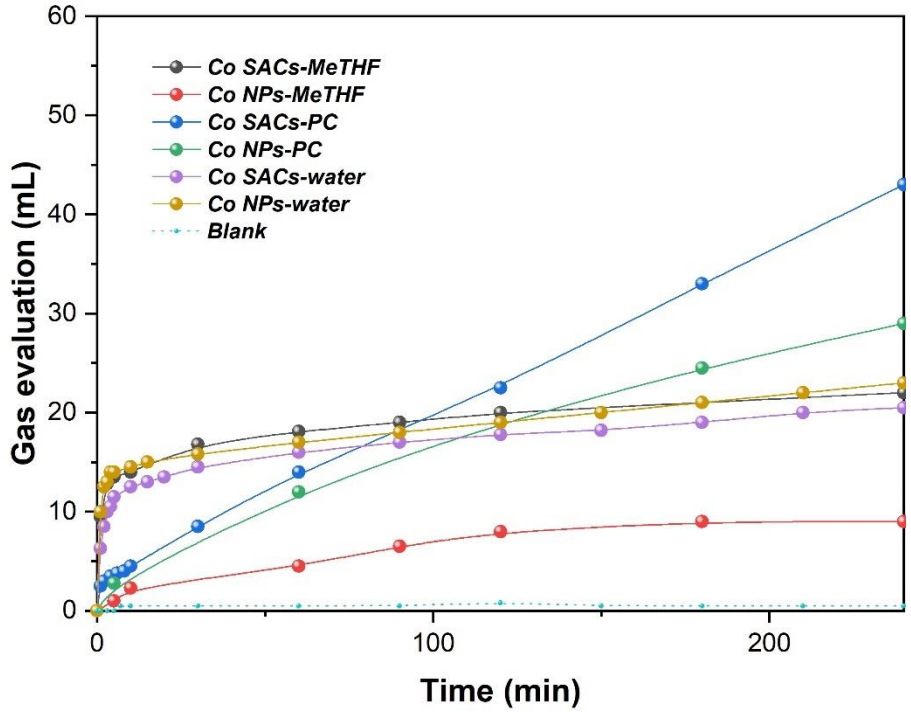
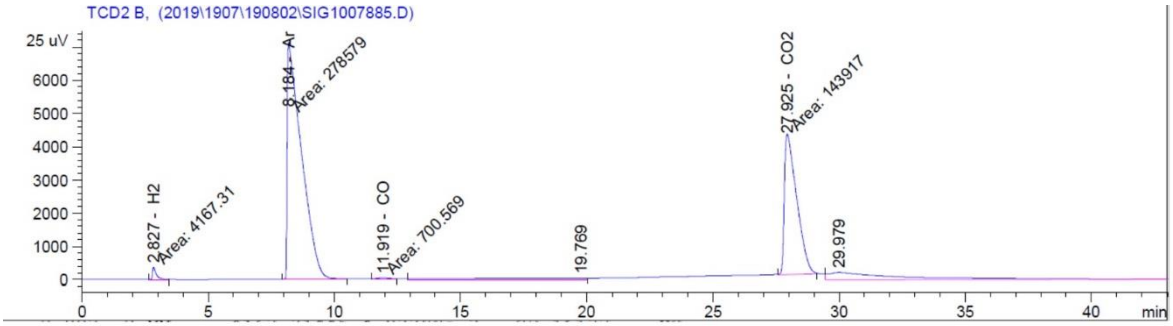


Figure S3. Investigation of the effect of solvent using on gas evaluation. Reaction conditions: FA (10 mmol) and catalyst (30 mg) in solvent (6 mL).

5.3 GC spectra



RetTime [min]	Sig	Type	Area	Amt/Area	Amount [vol%]	Grp	Name
2.827	2	MM	4167.31445	4.83798e-3	20.16137		H2
8.184	2	MM	2.78579e5	2.21258e-4	61.63780		Ar
11.919	2	MM	700.56860	2.22621e-4	1.55961e-1		CO
21.000	2		-	-	-		CH4
27.925	2	MM	1.43917e5	1.48831e-4	21.41930		CO2

Figure S4. GC spectra. Reaction conditions: HCOOH (10 mmol, 377 μL), Co-SACs (30 mg) in PC (6 mL), T_{set}: 110 °C, T_{actual}: 98 °C, 20 h.

Table S3. CO content and H_2 : CO_2 ratios for the DH of FA[a].

Experiment	V_{H2+CO2}[b] (mL)	H_2 Vol%[c]	CO_2 Vol%[c]	CO[c] (Vol%)	Vol%H_2 /(Vol% CO_2)	Time (h)
Co-N-C(SACs) /PC-110°C	140	48.3	51.3	0.37	0.94	20
Co-N-C(NPs) /PC-110°C	100	47.9	52	0.12	0.92	20
Co-N-C(SACs)/H_2O-100°C	52	40.1	59.9	0.06	0.67	20
Co-N-C(NPs)/H_2O-100°C	50	32.1	66.9	1.01	0.48	20
Co-N-C(SACs)/ MeTHF-85°C	22	n.d.	99.8	0.22	-	4
Co-N-C(NPs)/MeTHF-85°C	10	28	71.8	0.2	0.39	4
Co-N-C(NPs)/H_2O-100°C, neutral[d]	16	74.7	25	0.33	2.99	4
Co-N-C(NPs)/H_2O-100°C, Base[e]	12	94.4	5.6	n.d.	16.9	4
Co-N-C(NPs)/H_2O-100°C, $LiBF_4$[f]	19	58.8	41.1	0.11	1.43	4

[a]Reaction conditions detailed under the corresponding table/experiment in this work. [b]Gas evolution monitored with manual burettes. [c]Content of the gas phase analyzed by GC with a CO detection limit of 10ppm, n.d. stands for "not detected". [d] HCOONa is doped with a molar ratio to HCOOH is 32 to 5 to get a neutral condition with pH of 7. [e] KOH is doped with a molar ratio to HCOOH is 2 to 3 to get a base condition with pH of 14. [f] $LiBF_4$ is doped as additives with a 10% molar ratio.

6. Characterization of the Cobalt Catalyst

6.1 Elemental Analysis

Table S4. Elemental Analysis

Catalyst	EA (wt%)		
	Co	N	Co:N (molar ratio)
Co-N-C(SACs)-1000	1.355	6.619	0.2
Co-N-C(NPs)-800	39.36	2.033	19.4

6.2 XRD Measurements

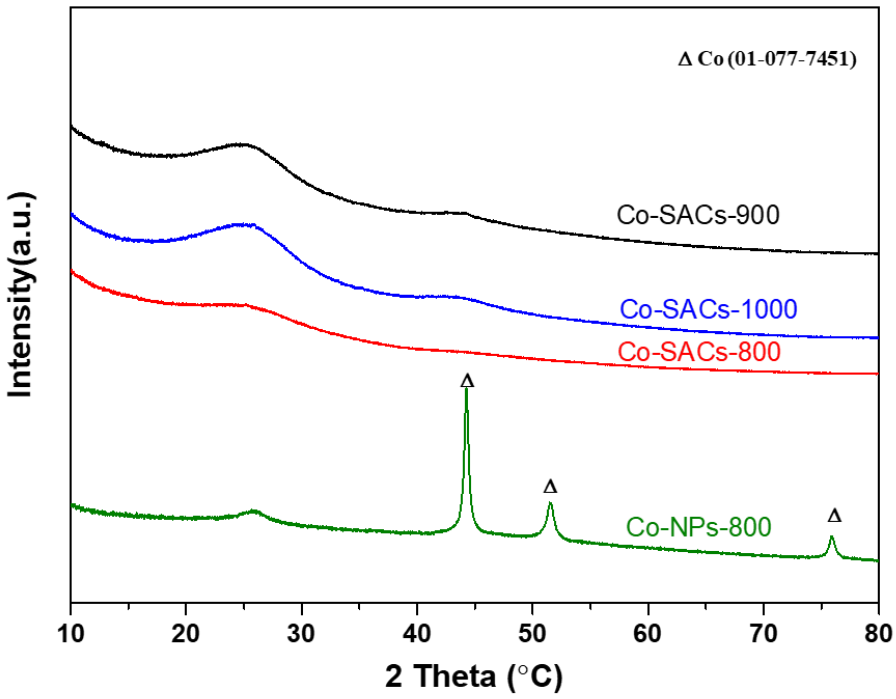


Figure S5. XRD spectra of the catalysts.

6.3 N_2 Adsorption Measurements

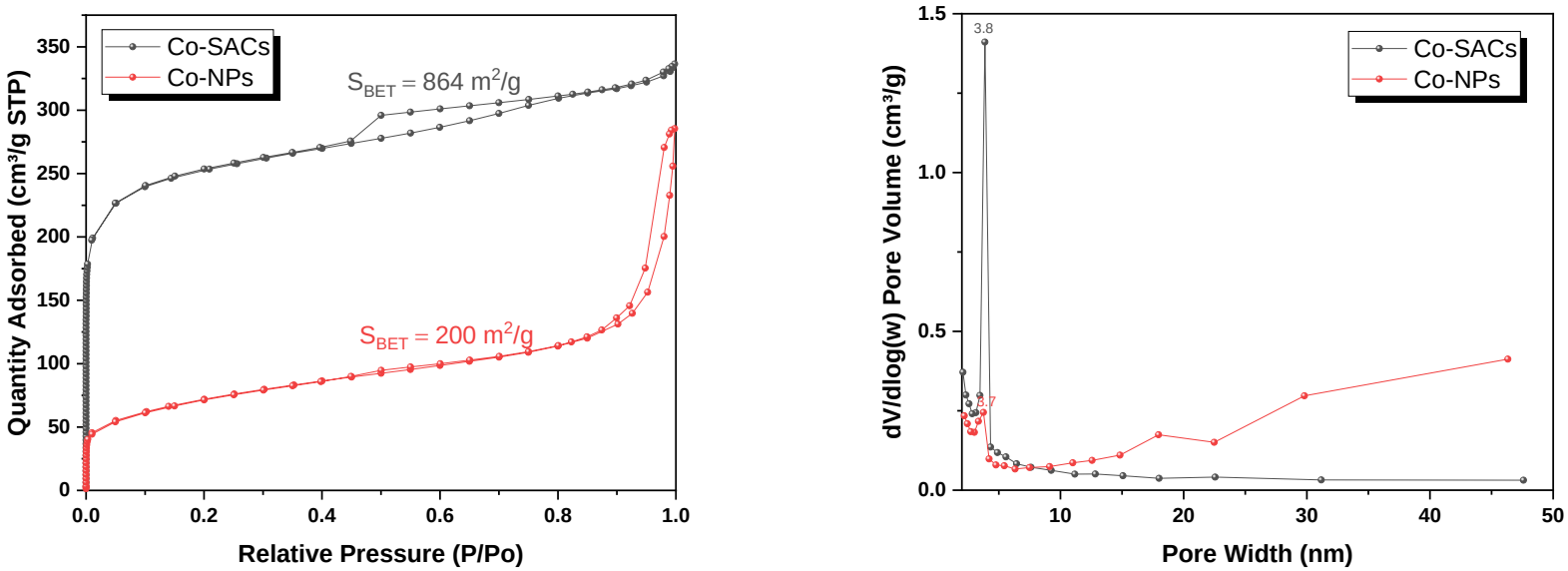


Figure S6. N_2 Adsorption isotherm (left) and pore size distribution (right) of the catalysts.

Co-N-C (SACs) catalyst has a quadruple BET surface area but similar pore size (~3.7 nm) to Co-N-C (NPs).

6.4 XPS results of catalysts

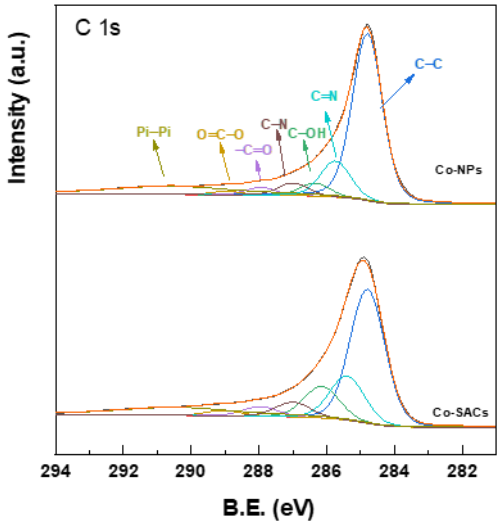


Figure S7. C1s xps curves of samples

Table S5. Surface concentration results by XPS

Catalyst	C-C (at%)	C=N (at%)	C-N (at%)	CO (at%)	OCO (at%)	Pi-Pi (at%)	C-OH (at%)	Total C (at%)	Pyridinic (at%)	Pyrrolic (at%)	Graphitic (at%)	N-O (at%)	Total N (at%)	Co (at%)
Co-N-C (SACs)	41.14	13.53	4.52	2.93	1.58	10.88	9.77	84.35	4.87	2.22	0.37	-	7.46	0.38
Co-N-C (NPs)	51.79	11.18	3.89	2.37	1.13	13.24	4.02	87.62	3.71	1.51	0.18	-	5.4	2.25

7. Test on the Stability of Active Sites for Co-N-C (SACs) and Co-N-C (NPs)

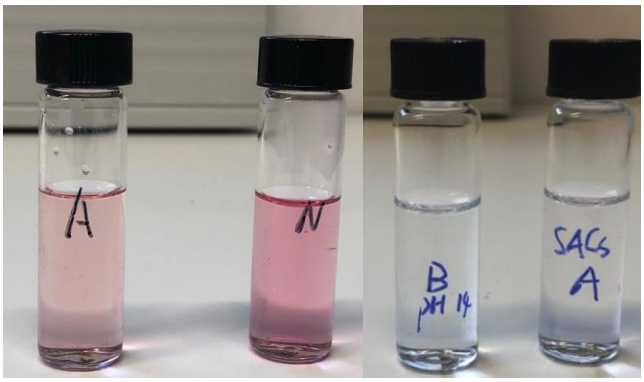


Figure S8. Colour change phenomenon of solvent after reaction (water as solvent): A for acidic condition (FA alone), N for neutral condition (FA/SA) and B for base condition (FA/KOH), left three are Co-N-C (NPs).

Figure S9. Phenomenon after reaction (water as solvent).

Figure S10. Phenomenon after reaction (PC as solvent).

Table S6. Co and N loss results after reaction by AAS

Catalyst	Solvent	Reaction time (min)	Color change	Co loss(%)	N loss(%)
Co-N-C (SACs)	PC	240	No	10.8	0.6
Co-N-C (NPs)	PC	240	No	38.1	41.5
Co-SACs	PC	7200	No	37	23.2
Co-NPs	PC	7200	No	49	61.1

8. Long-term Experiments

The reaction vessel was evacuated and refilled with argon for 6-8 times, FA (35 mmol, 1.32 mL) and PC (21 mL) were added to the vessel under argon flow, the thermostat was heated to the 110 °C (actual temperature 98 °C) and let equilibrate for 20 min. Then, the cobalt catalyst (30 mg) was added in a teflon crucible to the reaction vessel, setting this point as the starting point for measuring the evolved gas volume using a manual burette. The reaction was kept running for 120 h.

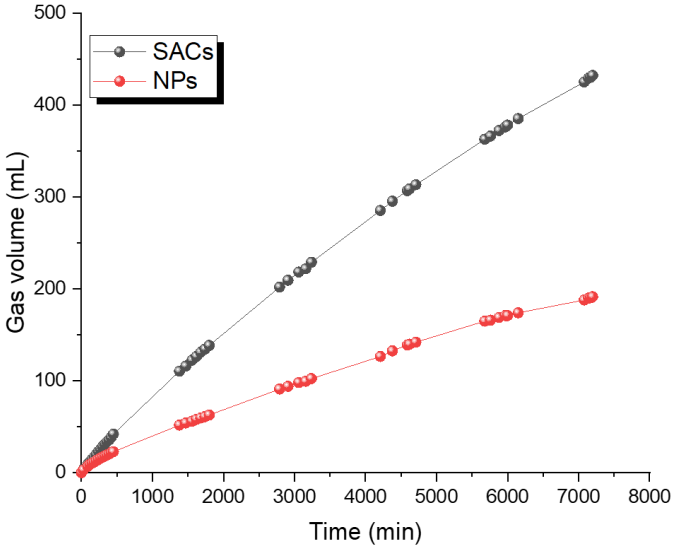


Figure S11. Long-term experiments.

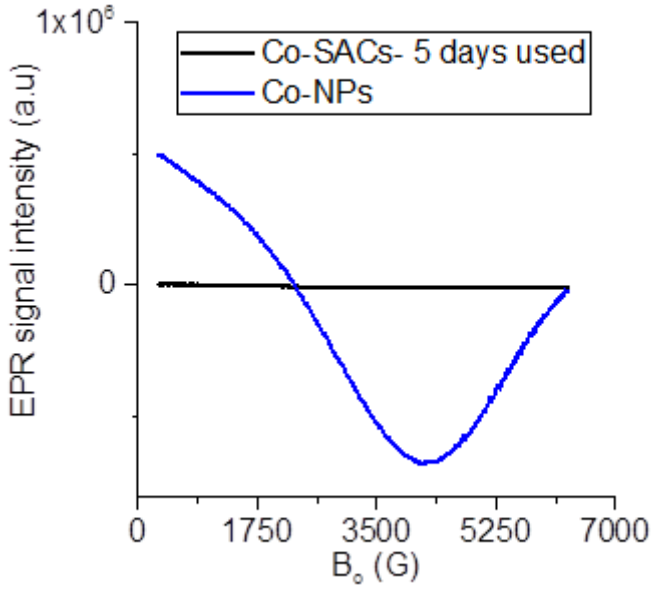


Figure S12. EPR spectra of Co-N-C(NPs) and Co-N-C(SACs) (after 7200h) measured at 100 K.

9. Fitting Results of EXAFS

Table S7. EXAFS fitting parameters at the Co K-edge for various samples（S_0^2=0.73）

Sample	Shell	N^a	R(Å)^b	$\sigma^2\times 10^3$(Å^2)^c	ΔE_0 (eV)^d	R factor
Co foil	Co-Co	12*	2.49±0.01	6.4±0.1	8.2±0.2	0.001
Co_3O_4	Co-O	4.3±0.4	1.92±0.01	3.0±0.3	-5.0±1.1	0.004
	Co-Co	2.7±0.5	2.85±0.01	2.0±0.9	-8.3±1.8	
	Co-Co	8.8±1.7	3.34±0.01	7.5±1.3	-9.7±1.6	
CoPc	Co-N	4.1±0.8	1.91±0.01	2.7±1.7	8.6±3.5	0.015
	Co-C	5.4±2.4	3.00±0.02	4.8±2.7	9.4±2.2	
Co samp	Co-N(O)	6.0±0.9	1.90±0.01	9.5±1.6	-6.7±2.0	0.011

[a]*N*: coordination numbers; [b]*R*: bond distance; [c]σ^2: Debye-Waller factors; [d] ΔE_0: the inner potential correction. *R* factor: goodness of fit.

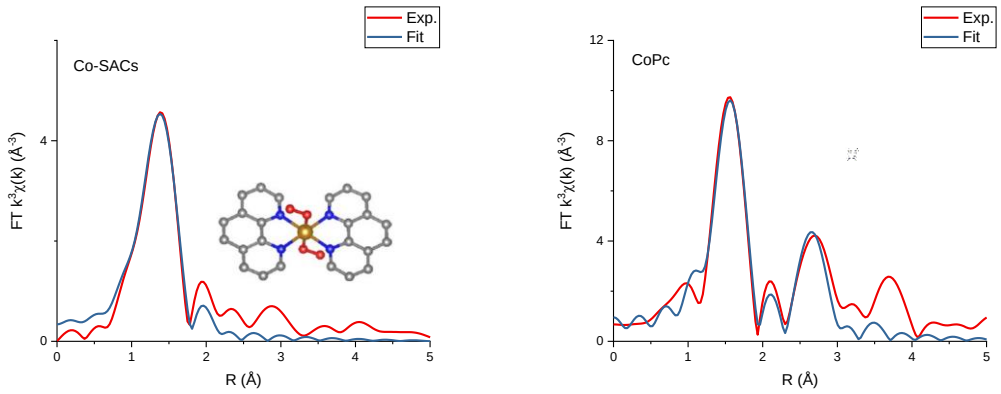


Figure S13. Fitting EXAFs spectrum of Co-N-C(SACs) and CoPc.

10.TEM

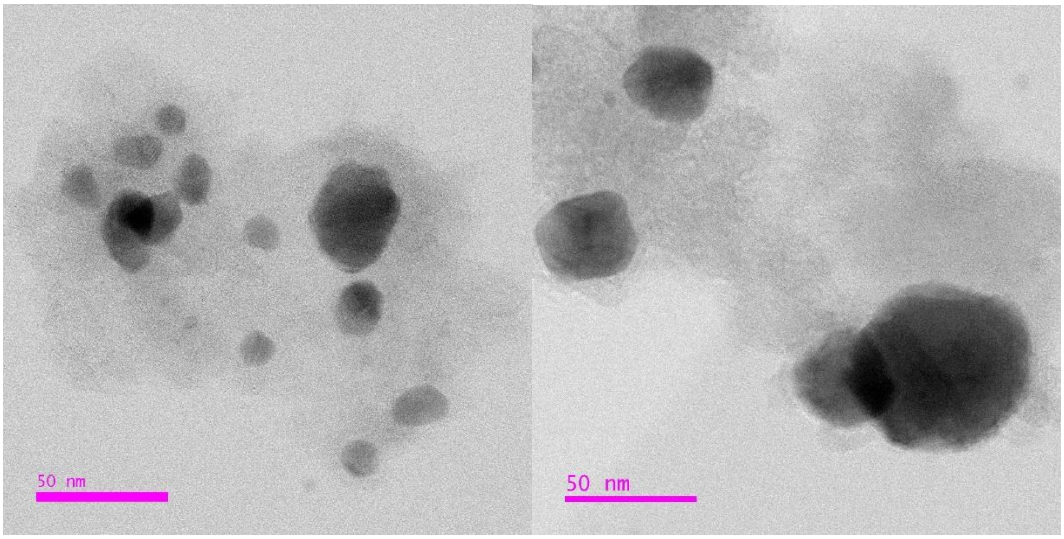


Figure S14. HRTEM images of Co-N-C(NPs)-900 (left) and Co-N-C(NPs)-1000 (right).

11.NMR

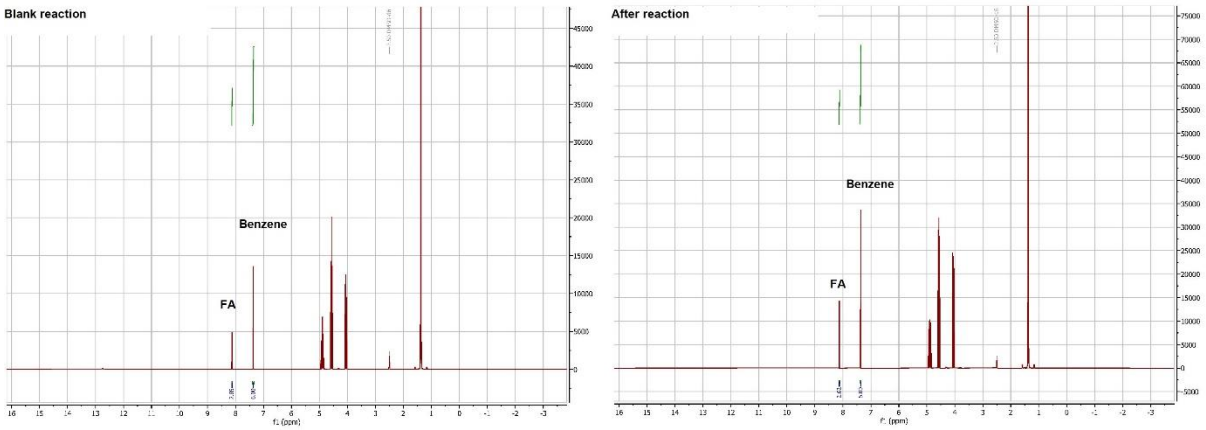


Figure S15. The NMR curves of blank (left) and end of reaction (right) with benzene as an inner standard.

12. Mechanistic Proposal for Formic Acid Dehydrogenation

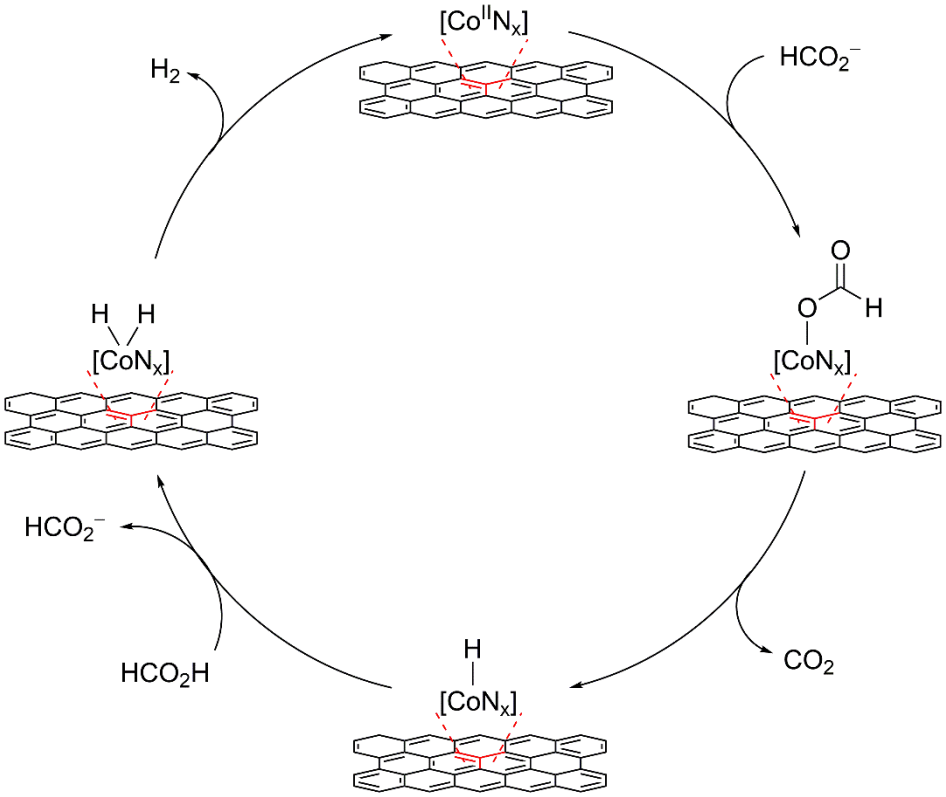


Figure S16. A general mechanistic proposal for formic acid dehydrogenation by Co-N-C(SACs) catalysts.

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