Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Nanoporous Nickel catalyst for selective hydrogenation of carbonates into formic acid in water

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Calculation of TON and TOF

The methods to measure TOF and TON are as follows:

$$\text{TOF } (h^{-1}) = \frac{\text{The amount of Formic formed, } \textit{mmol per hour}}{\text{The amount of catalyst, } \textit{mmol}}$$

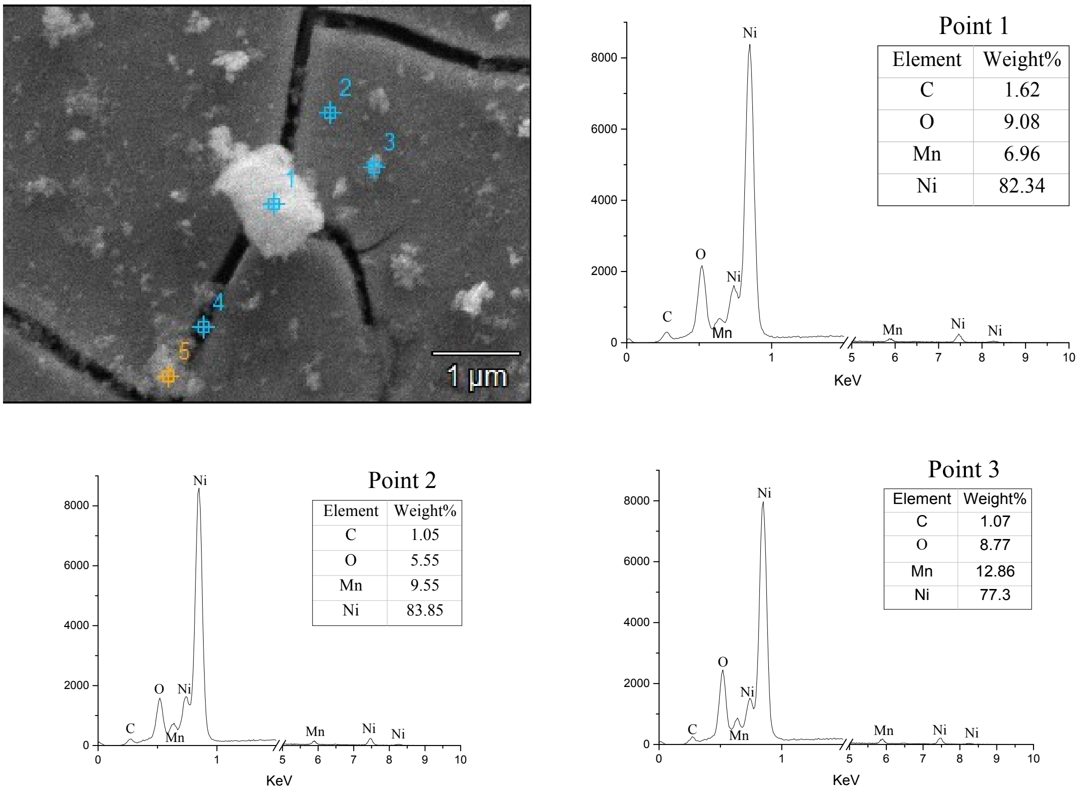
$$\text{TON} = \frac{\text{The amount of Formic formed, } \textit{mmol}}{\text{The amount of catalyst, } \textit{mmol}}$$

Based on previous literature [1], we also assume that every surface atom is an active site as an upper limit. For the energetically most stable Ni (111) surface, the density of surface atoms is $1.86*10^{19}$ atoms/m^2. And the specific surface area of NiNPore is 62.1 m^2/g. Then the TOF can be calculated using these values as follows:

$$\text{TOF}=\frac{86.68\ mmol}{\dfrac{1.86\times10^{19}\ atoms/m^2\times62.1\ m^2/g\times13\ mg}{6.02\times10^{23}/mol}\times2\ h}\approx1738\ h^{-1}$$

$$\text{TON}=3476$$

Scheme 1. Calculation of TOF and TON



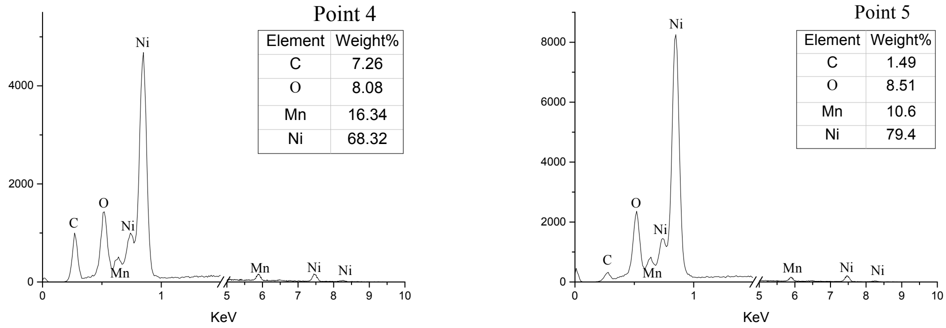


Figure SI-1. Energy Dispersive Spectroscopy (EDS) of fresh NiNPore catalyst.

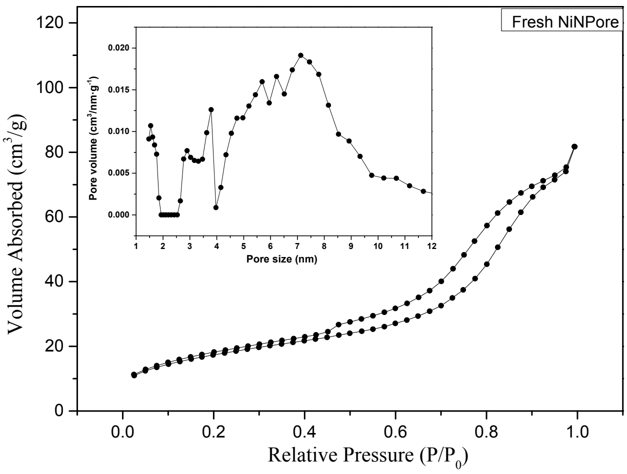


Figure SI-2. Nitrogen adsorption/desorption isotherm and corresponding pore size distribution curve (inset) of fresh NiNPore.

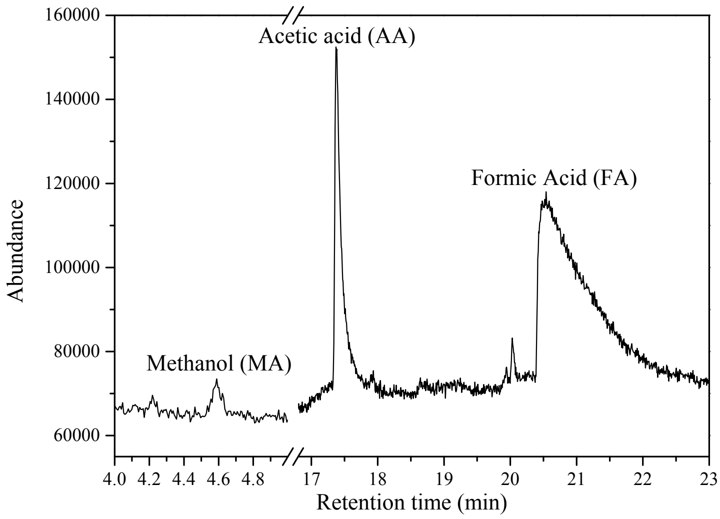


Figure SI-3. GC-MS spectrum of liquid samples.

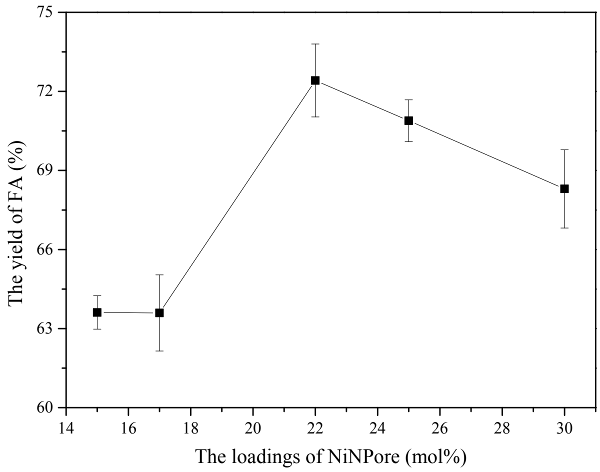


Figure SI-4. Effect of NiNPore loading on FA yield.

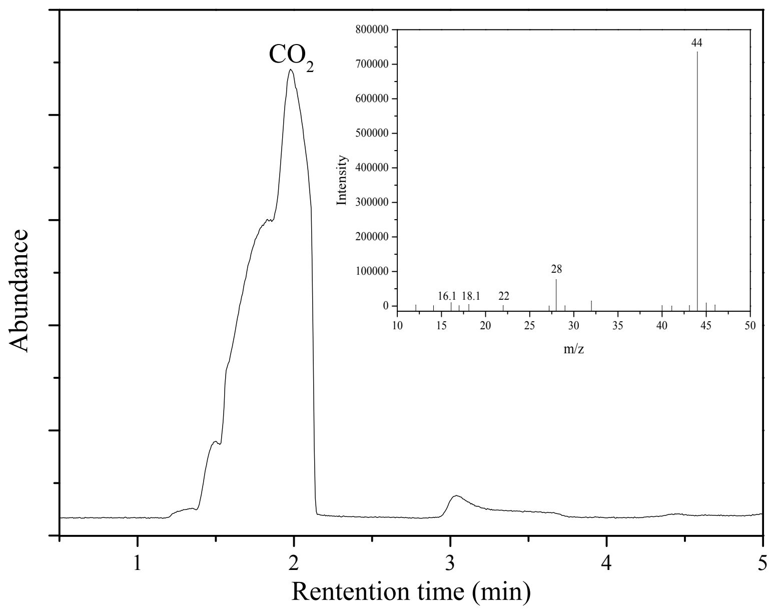


Figure SI-5. GC-MS spectrum of confirmed CO_2 (Conditions: HCOONa 1 mmol, NiNPore 15 mol%, H_2 3 MPa, H_2O 10 mL, 200 ^oC, 2 h).

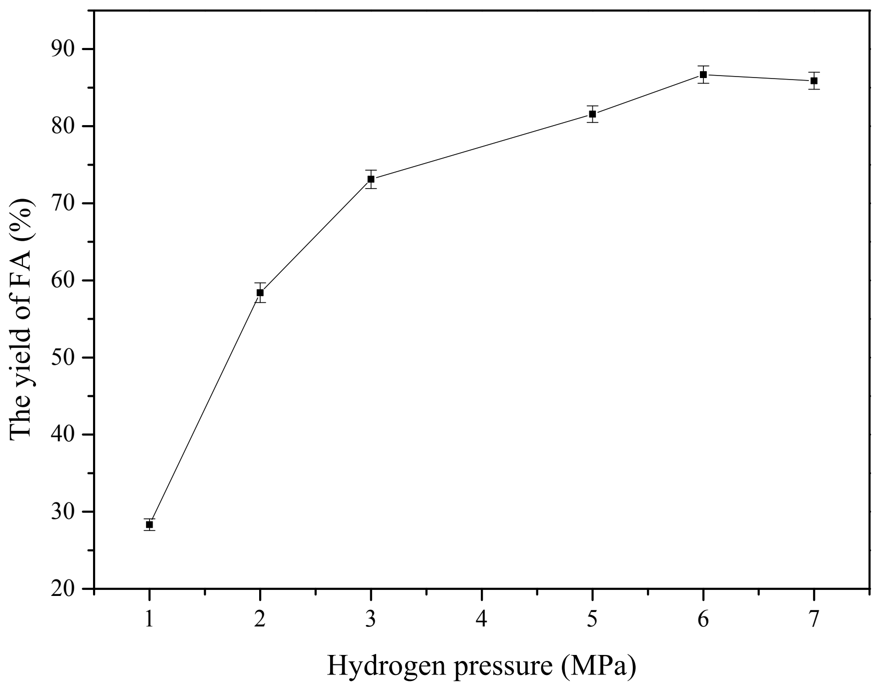


Figure SI-6. Effect of hydrogen pressure on FA yield.

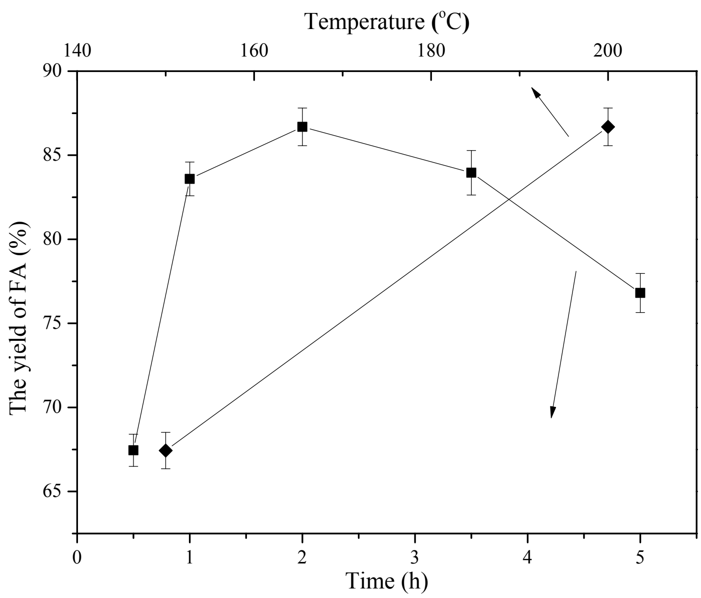


Figure SI-7. Effect of temperature and reaction time on FA yield.

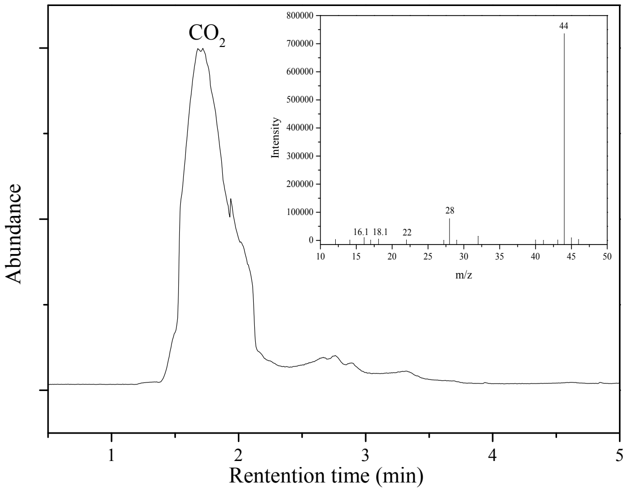


Figure SI-8. GC-MS spectrum of confirmed CO_2 (Conditions: HCOONa 1 mmol, NiNPore 22 mol%, H_2 6 MPa, NEt_3 2mmol, H_2O 10 mL, 200 ^oC, 2 h).

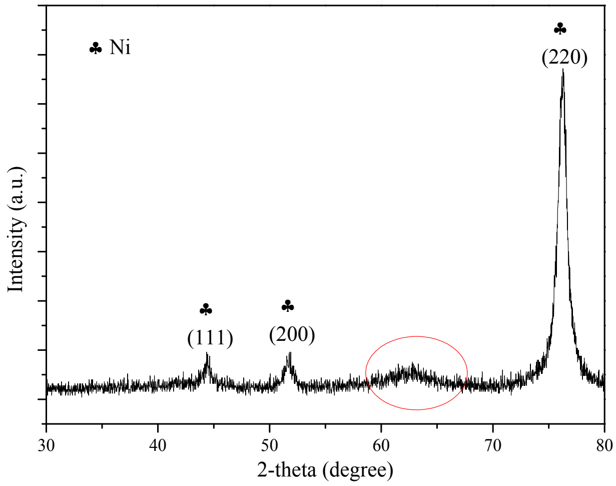


Figure SI-9. XRD patterns of fresh NiNPore.

Table SI-1. Structural information of catalysts

Catalyst	Particle size	Surface area (m^2/g)	Pore size	FA yield (%)[a]
NiNPore	-	62.11	7.1 nm	63.2
Raney Ni	-	15.29	~5 nm	60.1
Al-Ni alloy	-	4.32	-	56.5
NiO	-	3.91	-	3.5
Ni power	200 mesh	2.63	-	1.8

[a] Reaction conditions: $NaHCO_3$ 1 mmol, NiNPore 17 mol%, H_2 3 MPa, H_2O 10 mL, 200 ^oC, 2 h.

Table SI-2. Effect of catalyst loading on FA decomposition.[a]

Entry	Catalyst loading (mol%)	Residual HCOONa (mmol/L)
1	15	62.4
2	17	61.3
3	22	59.6
4	25	57.3

[a] Reaction conditions: HCOONa 1 mmol (100 mmol/L), H_2 3 MPa, H_2O 10 mL, 200 ^oC, 2 h.

Table SI-3. Effect of NEt_3 on FA decomposition.

Entry	H_2 Pressure	Additive	Residual HCOONa (mmol/L)
1	6		78.7
2	6	NEt_3 (2 mmol)	68.7

Conditions: HCOONa 1 mmol, NiNPore 22 mol%, H_2O 10 mL, 200 ^oC, 2 h.

Table SI-4. Ni 2p3/2 spectral fitting parameter and the ratio of Ni, NiO and $Ni(OH)_2$ on catalyst surface.

Catalyst	Ni $2p_{3/2}$ Peak position (eV) [2, 3]			Ratio (%)			FA yield [a]
	Ni	NiO	$Ni(OH)_2$	Ni	NiO	$Ni(OH)_2$	(%)
Fresh				9.8	24.3	65.9	86.6
1st cycle	852.6	860.9	854.9	20.5	19.3	60.2	87.9
5th cycle				25.6	17.7	56.7	90.5

[a] Condition: $NaHCO_3$: 1 mmol, NiNPore: 22 mol%, H_2: 6 MPa, Solvent: H_2O 10 mL, 200 ^oC, 2h.

Table SI-5. Investigation of decomposition of HCOONa and $HCOONH_4$.

Entry	material	Residual (mmol/L)
1	HCOONa	78.7
2	$HCOONH_4$	35.8

Conditions: feedback 1 mmol, NiNPore 13 mg, H_2 6 MPa, H_2O 10 mL, 200 ^oC, 2 h.

Reference:

1. A. Wittstock, V. Zielasek, J. Biener, C. M. Friend and M. Baumer, *Science*, 2010, **327**, 319-322.
2. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717-2730.
3. A. P. Grosvenor, M. C. Biesinger, R. S. C. Smart and N. S. McIntyre, *Surf. Sci.*, 2006, **600**, 1771-1779.