Supplementary materials

Selective hydrogenation of CO_2 to formic acid with higher yield in an aqueous medium with a nano-nickel-metal catalyst: reaction parameter optimization by response surface methodology (RSM)

Rajeev Ranjan, Prakash Biswas*, and K. K. Pant

Affiliation

Department of Chemical Engineering, Indian Institute of Technology Roorkee,

Roorkee-247667, Uttarakhand, India

*Corresponding author: Tel.: (+91)-1332-28-5820

Email: prakash.biswas@ch.iitr.ac.in; prakashbiswas@gmail.com

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1. N_2 adsorption-desorption isotherm of nano-nickel catalyst

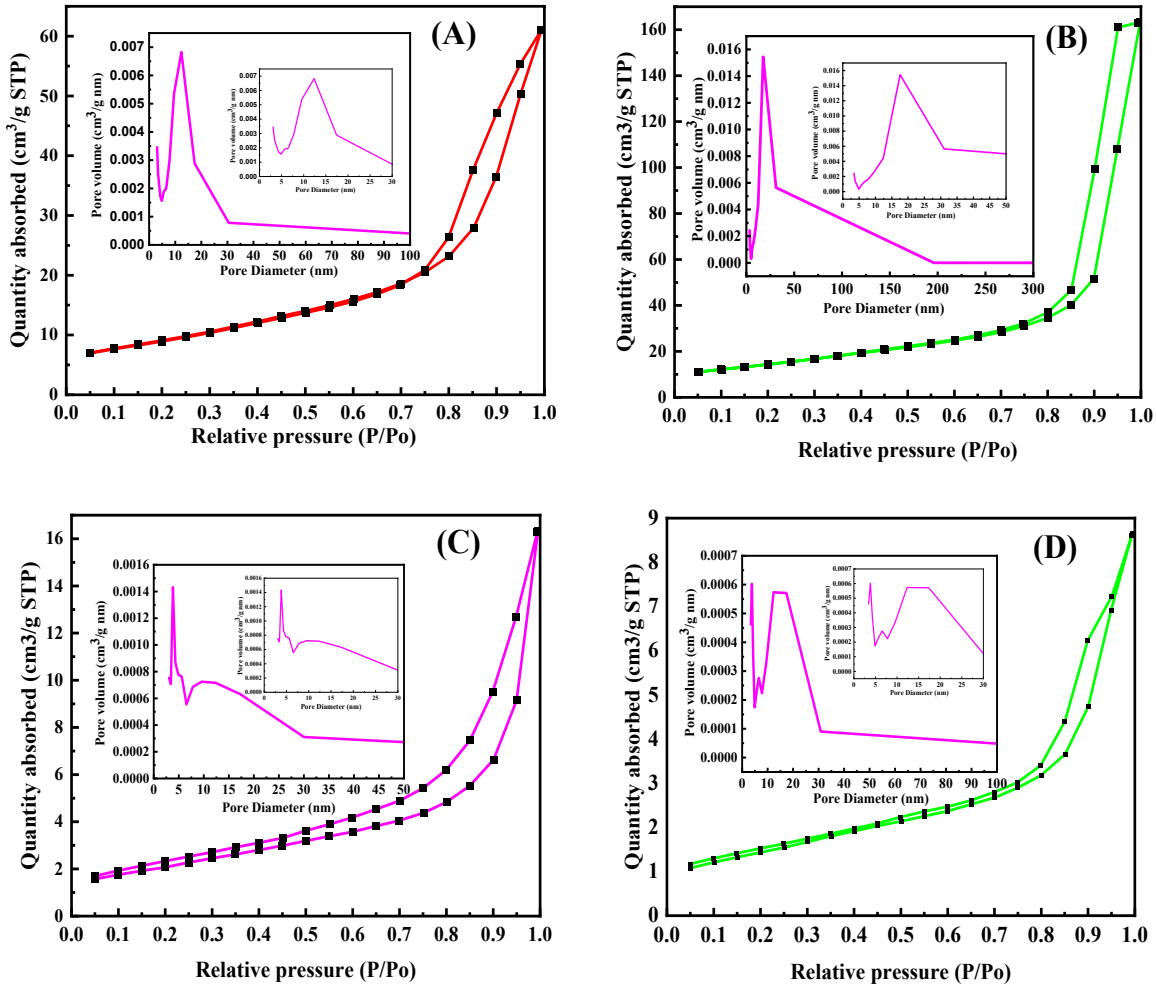


Figure S1. N_2 adsorption-desorption isotherm of nano-nickel catalyst (a) NiO-PM, (b) NiO-HT, (c) NiO-SG, (d) NiO-DC.

2. FTIR spectrum of NiO-SG catalyst

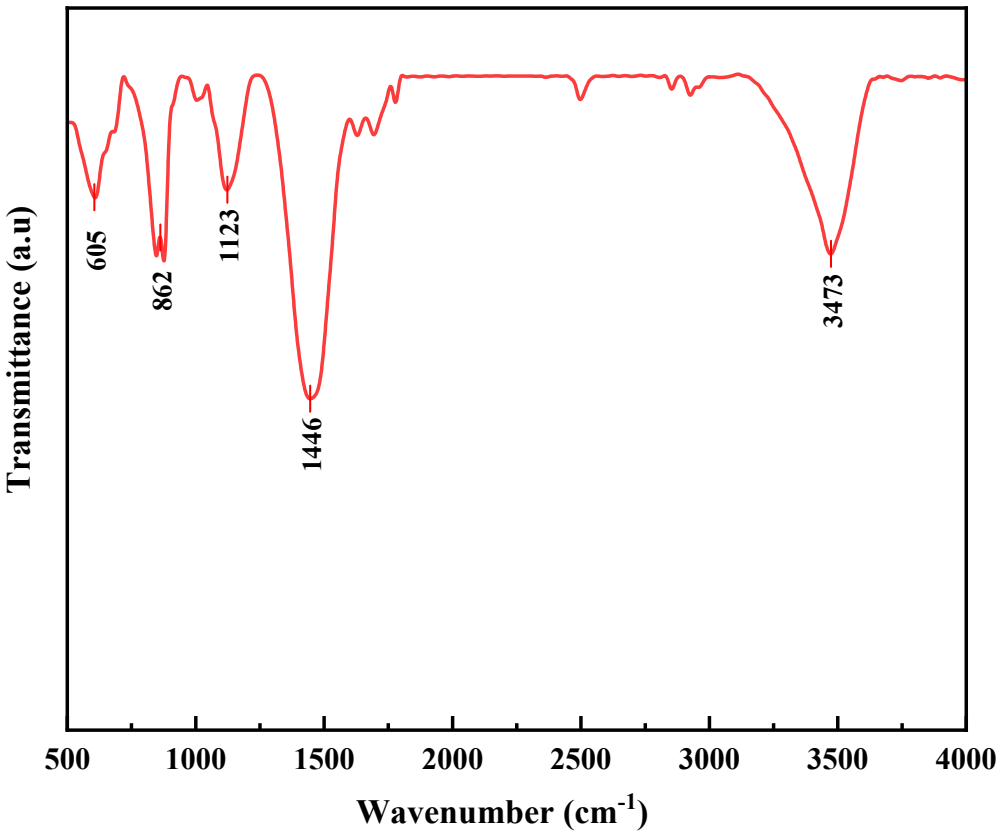


Figure S2. FTIR spectra of NiO-SG catalyst[1,2].

3. DR-UV-vis spectra of NiO-SG catalyst

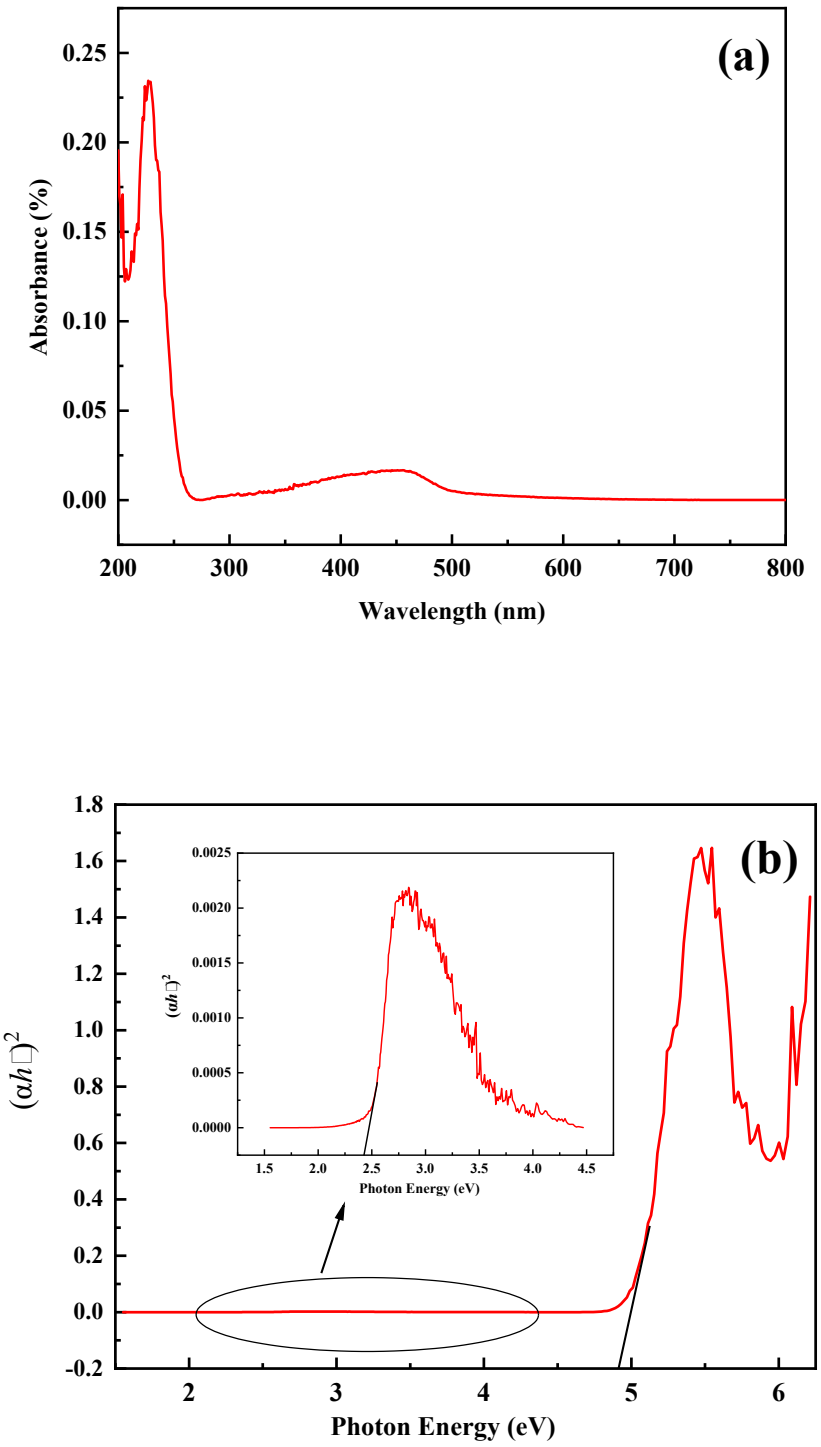
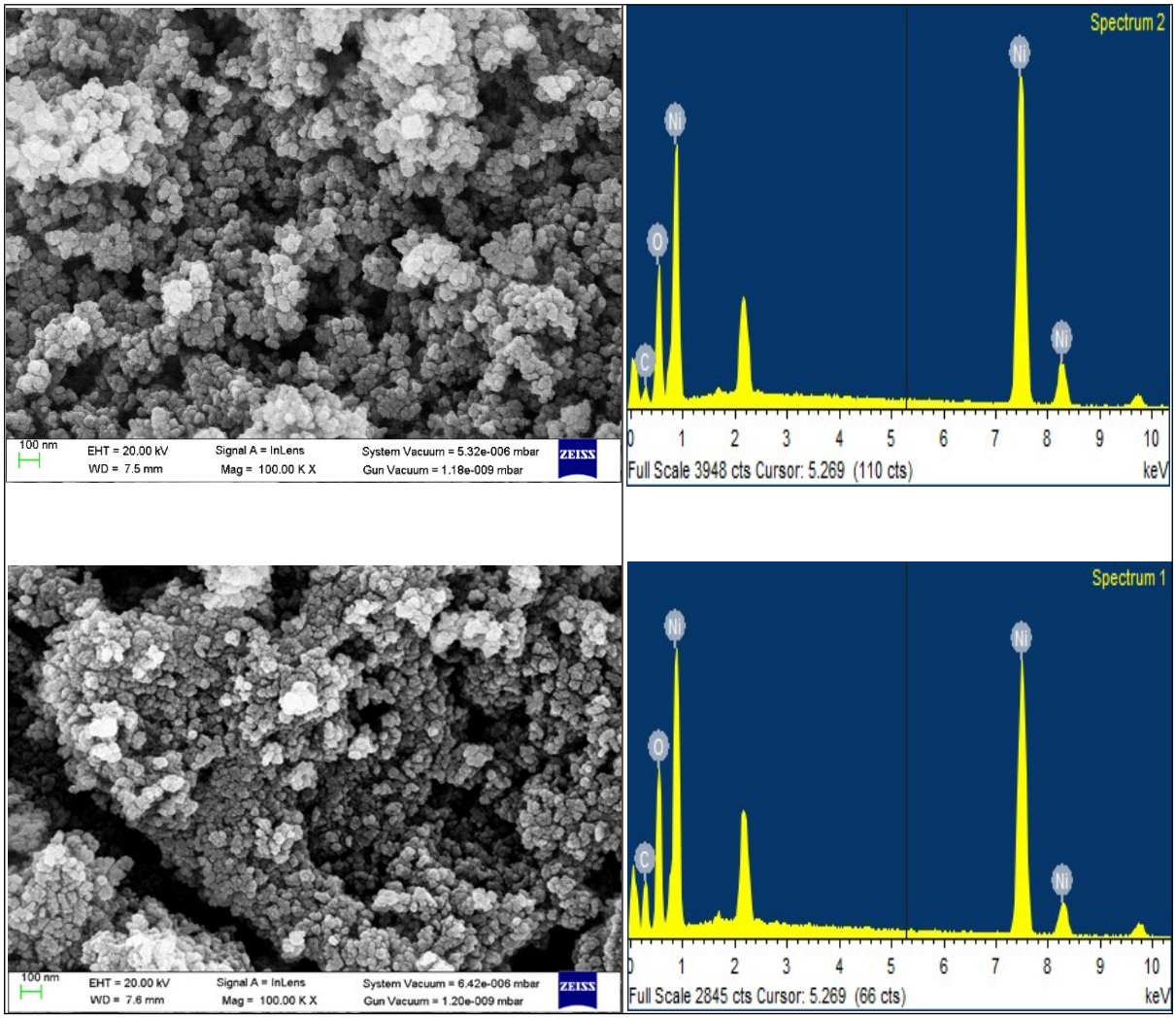


Figure S3. (a) UV-vis diffuse reflectance spectra (DRS) of NiO-SG catalyst, (b) Tauc plot of NiO-SG catalyst[3,4].

4. FE-SEM images with EDX of catalysts



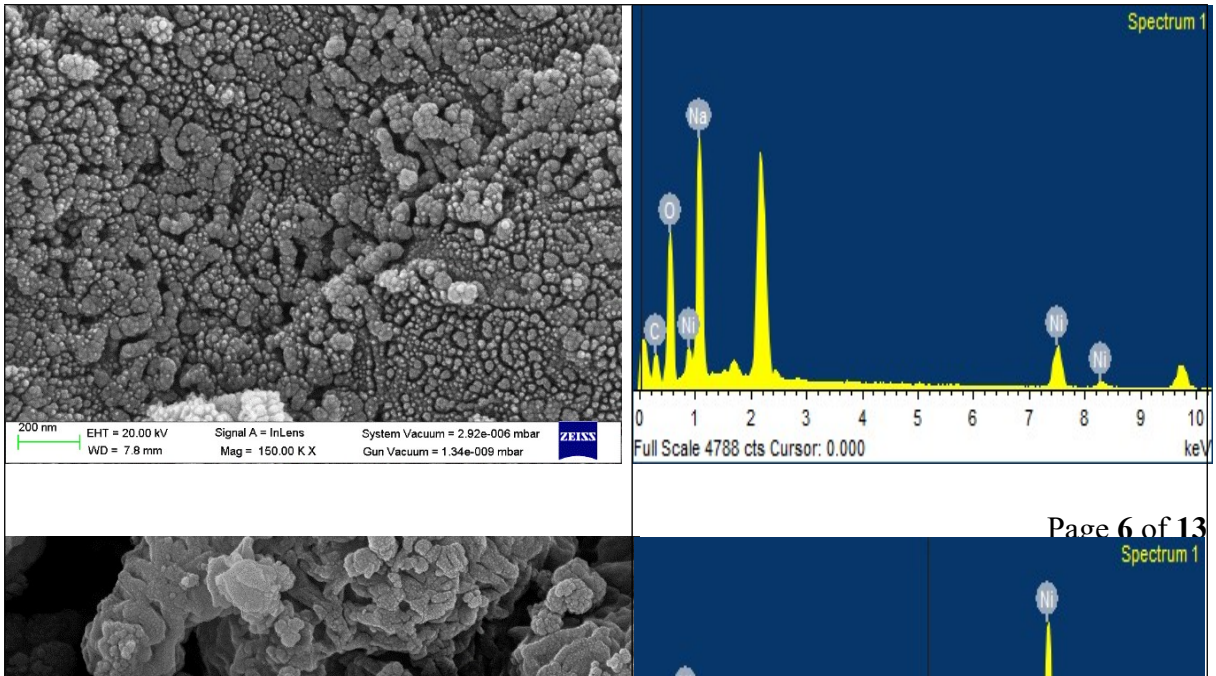


Figure S4. FE-SEM images with EDX of (A) NiO-PM, (B) NiO-PM EDX, (C) NiO-HT, (D) NiO-HT EDX, (E) NiO-SG, (F) NiO-SG EDX, (G) NiO-DC (H) NiO-DC EDX.

5. Catalyst screening for the CO_2 hydrogenation to formic acid

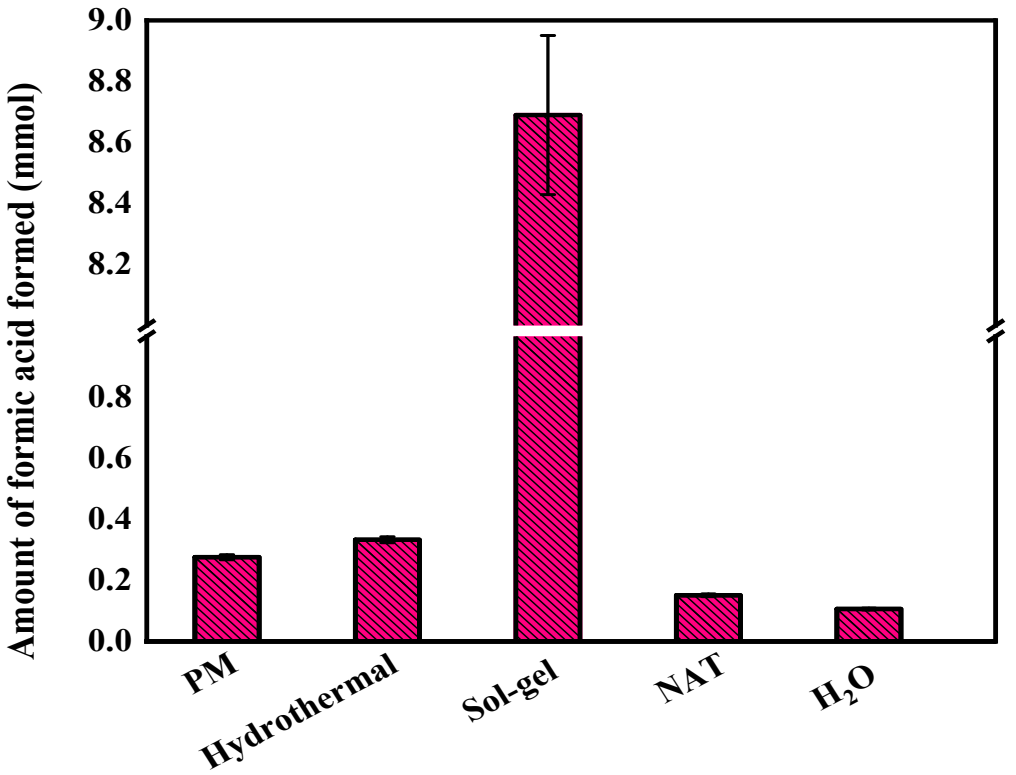


Figure S5. CO_2 hydrogenation to formic acid over various catalysts

Reaction condition: 200 ^oC, 60 bar pressure, 1 g catalyst, water as solvent.

6. ^1H NMR of the reaction mixture

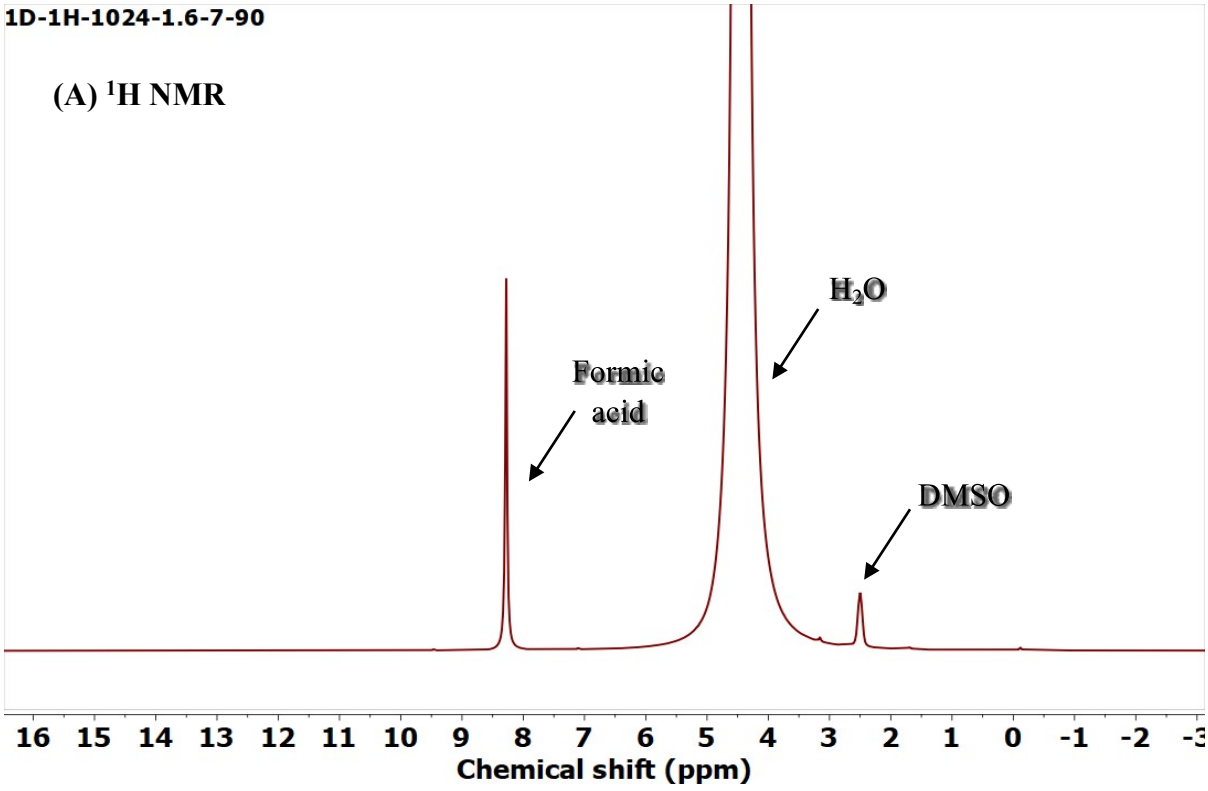


Figure S6. (A) ^{1}H NMR of the reaction mixture with DMSO-d6 as a reference[5–7].

7. XRD pattern of nano-nickel catalyst

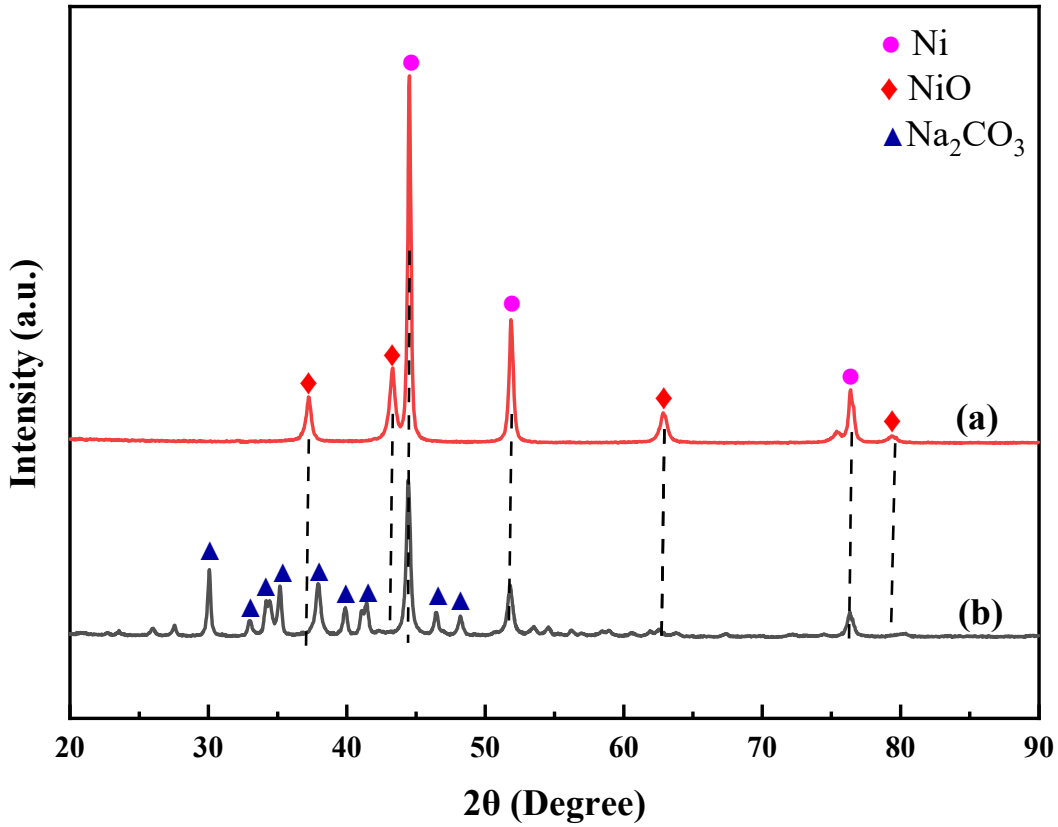


Figure S7. XRD pattern of nano-nickel catalyst (a) NiO-R1, (b) NiO-SG.

8. Formic acid yield for recycles experiments.

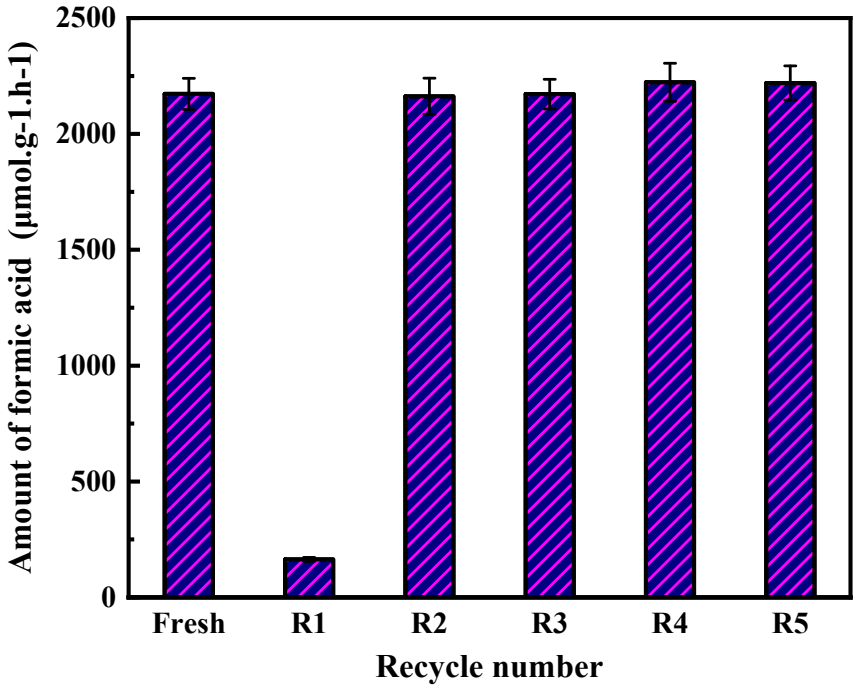


Figure S8. Formic acid yield in the recycles experiments.

9. Results obtained from CO_2-TPD for basic sites

Table S1. Results obtained from CO_2-TPD for basic sites

Catalyst	Weak base (mmol/g-cat)	Moderate base (mmol/g-cat)	Strong base (mmol/g-cat)	Total basic strength (mmol/g-cat)
NiO-PM	0.0012	0.0033	0.0056	0.0101
NiO-HT	0.0012	0.0080	0.0133	0.0225
NiO-SG	-	-	0.1079	0.1079
NiO-DC	0.0010	0.0006	0.0020	0.0036

10. Selected factors with their corresponding coded values

Table S2. Selected factors with their corresponding coded values

Factor	Name	(-α)	-1	0	+1	(+α)
A	Temperature (°C)	20.00	50.00	125.00	200.00	230.00
B	Catalyst loading (g)	0.0400	0.20	0.60	1.00	1.16
C	Feed ratio P(CO_2/H_2)	0.2000	0.50	1.25	2.00	2.30

References

1 S. Yin, Y. Zeng, C. Li, X. Chen and Z. Ye, .

2 S. Joshi, S. Kalyanasundaram and V. Balasubramanian, *Appl. Spectrosc.*, 2013, **67**, 841–845.

3 U. Baig, A. Khan, M. A. Gondal, M. A. Dastageer and W. S. Falath, *Nanomaterials*, , DOI:10.3390/nano10061098.

4 N. Duraisamy, K. Kandiah, R. Rajendran, S. Prabhu, R. Ramesh and G. Dhanaraj, *Res. Chem. Intermed.*, 2018, **44**, 5653–5667.

5 Ö. Coşkuner, C. A. Castilla-Martinez, O. Sonzogni, E. Petit, U. B. Demirci and A. Kantürk Figen, *Int. J. Hydrogen Energy*, , DOI:10.1016/j.ijhydene.2021.12.236.

6 C. Fletcher, Y. Jiang and R. Amal, *Chem. Eng. Sci.*, 2015, **137**, 301–307.

7 B. D. Bankar, K. Ravi, R. J. Tayade and A. V. Biradar, *J. CO2 Util.*, 2023, **67**, 102315.