Electronic Supplementary Information

Molecular H_2O promoted catalytic bicarbonate reduction with methanol into formate over $Pd_{0.5}Cu_{0.5}/C$ under mild hydrothermal conditions

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Experimental Section

Analytical methods

HPLC analysis was performed on an Agilent 1200 system, which is equipped with two KC-811 columns (SHODEX) for samples separation and a tunable UV/Vis absorbance detector adjusted at 210 nm for samples detection. A 2 mmol/L $HClO_4$ solution with a flow rate of 1.0 mL/min was used as the mobile phase.

QNMR analysis was performed on a Bruker Avance III 600 MHz NMR-Spectrometer, and the quantitative estimation of products concentration was obtained using internal standard method and reported results were based on the average values of at least three samples according to our previous works.[S1]

For GC-MS analysis, a Hewlett-Packard model 7890A gas chromatograph system equipped with a model 5975C mass selective detector was used. The initial oven temperature in the gas chromatograph was 313 K, which was kept for 1 min, and then procedurally increased at a rate of 7 ^{o}C/min to a final temperature of 503 K and was held for 20 min. Samples were separated with a HP-INNOWAX polar capillary column (25 m long, 0.25 mm i.d., 0.5 μm film thickness) using helium as the carrier gas.

Gas samples were analyzed by a Hewlett-Packard model 5890 Series II Plus gas chromatograph (GC-TCD) equipped with a packed column (TDX-01) using N_2 as the carrier gas.

X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6100 PC with a Cu Kα radiation (λ = 1.54184 Å) in steps of 0.02° and an accumulation time of 0.6 s per step from 10 to 80° at 40 kV and 40 mA.

Transmission electron microscope (TEM) photographs were taken on JEOL JEM-2100F at an acceleration voltage of 200 Kv, and the sample stage is copper mesh ultra-thin carbon film.

Definition

'Formate production efficiency' was used to evaluate the efficiency of $HCO_3^{-}/CO_3^{2-}/CO_2$ reduction with alcohol, which was defined as follow:

$$Formate\ production\ efficiency\ (\%) = \frac{Produced\ formate\ from\ carbon\ source\ (mmol\ L^{-1})}{Initially\ added\ alcohol(mmol\ L^{-1})} \times 100\%$$

The $HCO_3^{-}/CO_3^{2-}/CO_2$ generated formate was quantified by ^{13}C-qNMR with $CH_3{}^{13}\underline{C}OOH$ added to the samples as an internal standard since the -COOH group in $H^{13}\underline{C}OOH$ and $CH_3{}^{13}\underline{C}OOH$ has the nearest sensitivity in ^{13}C-qNMR.

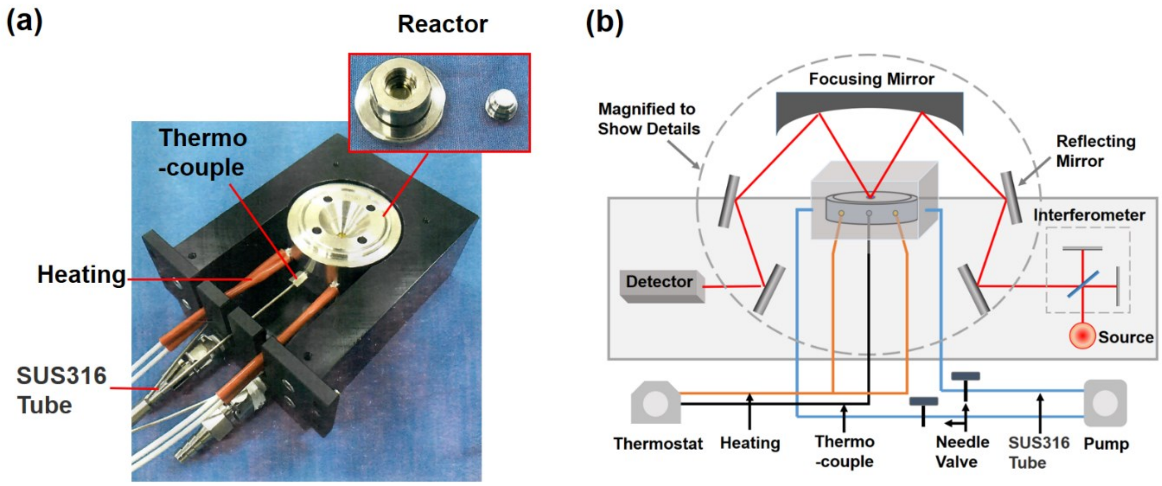

Fig. S1 Schematic drawing of *operando* hydrothermal ATR-FTIR ((a) photo of high-temperature and high-pressure ATR-FTIR reactor; (b) schematic drawing of whole system of operando high-temperature and high-pressure ATR-FTIR).

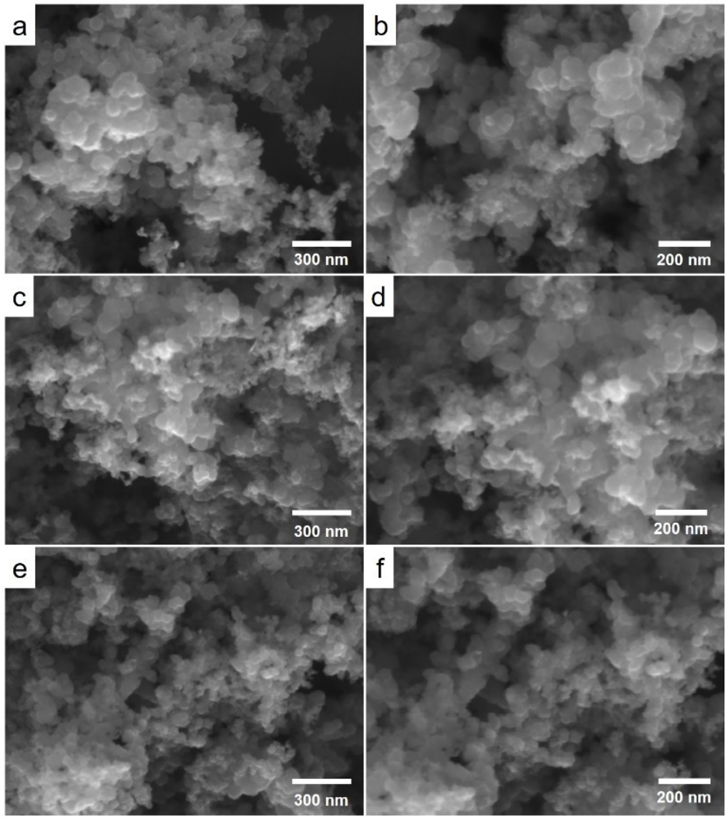

Fig. S2 SEM images of the as-prepared Pd/C (a, b), $Pd_{0.5}Cu_{0.5}/C$ (c, d) and carbon black (e, f).

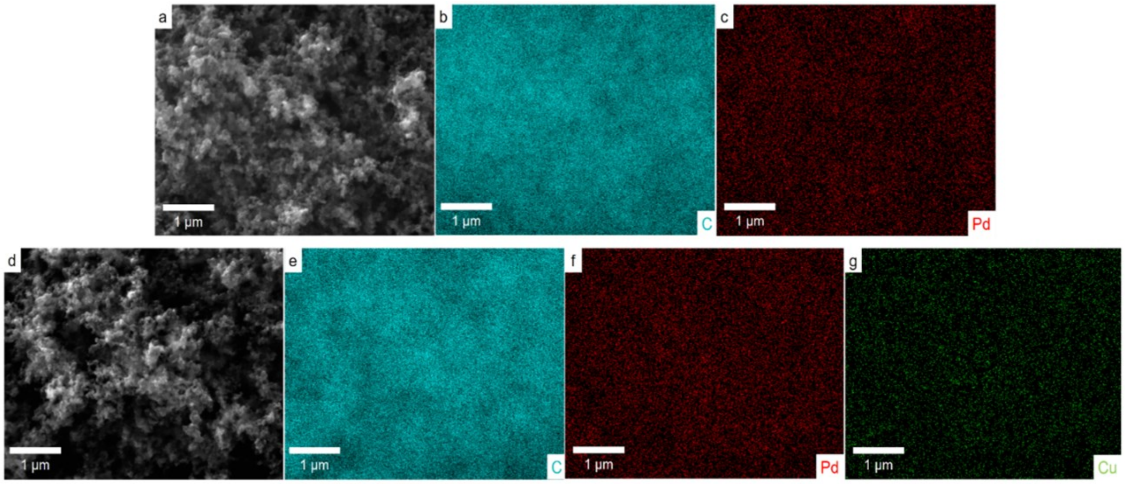

Fig. S3 SEM-EDS images of the as-prepared Pd/C (a-c) and Pd0.5Cu0.5/C (d-g).

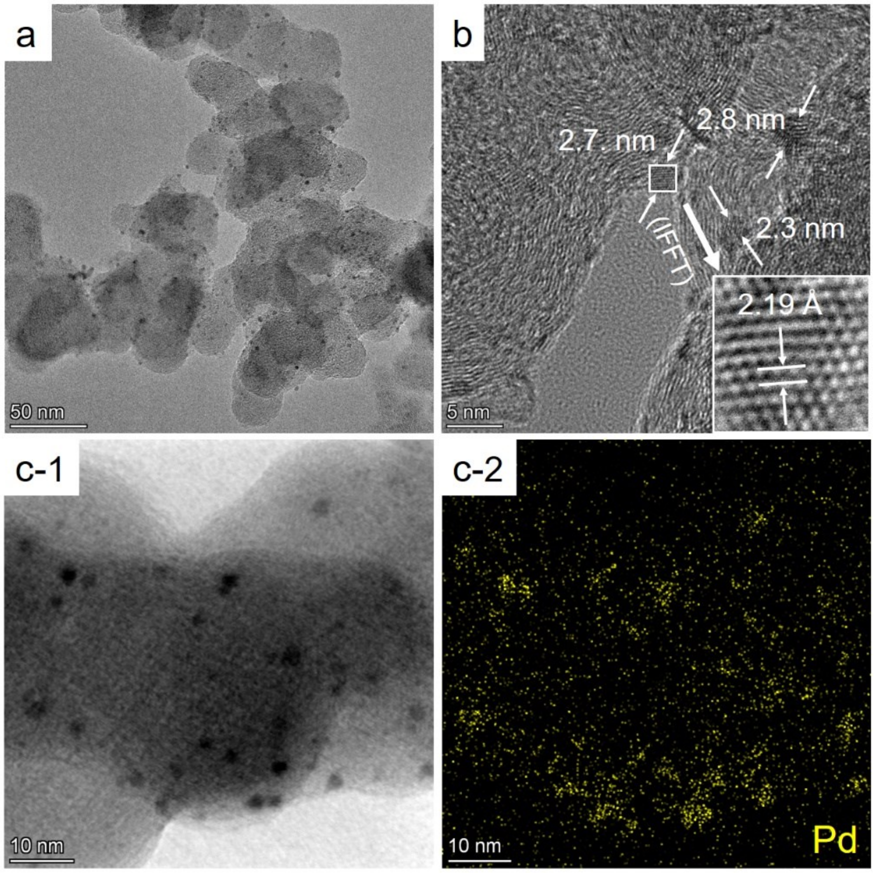

Fig. S4 TEM images (a), HRTEM image (b), and TEM-EDS elemental mapping (c) of the as-prepared Pd/C.

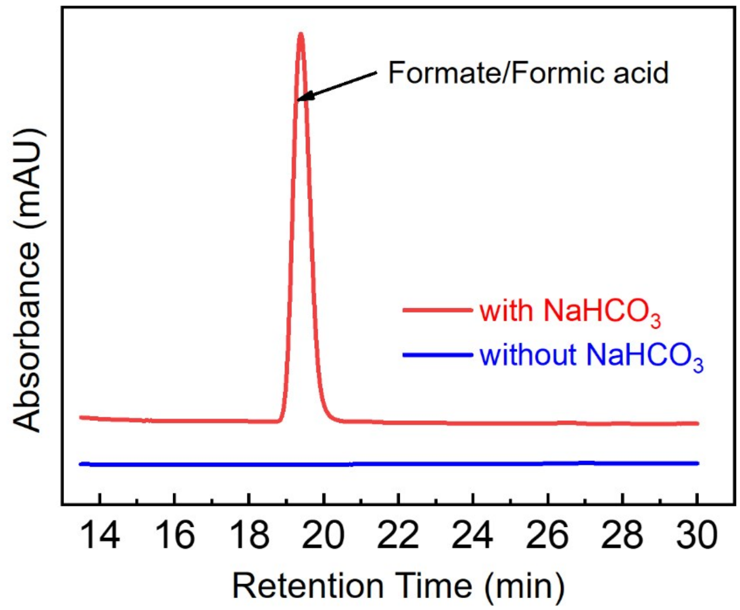

Fig. S5 HPLC chromatograms of methanol reacting with or without $NaHCO_3$ (reaction conditions: 0.1 mol/L CH_3OH, 1 mol/L $NaHCO_3$, 50% water filling, 180 ºC, and 16 h).

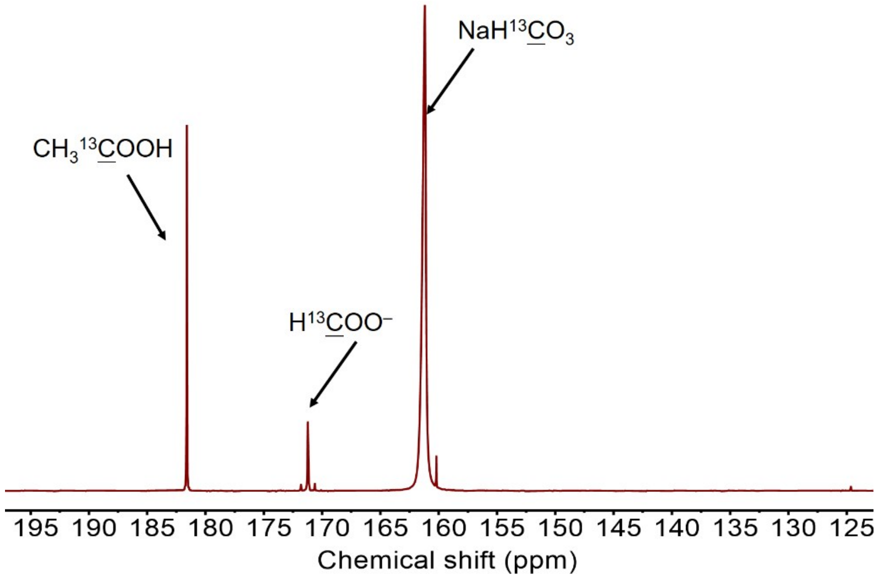

Fig. S6 ^{13}C-qNMR of the liquid sample after the reaction of $NaH^{13}\underline{C}O_3$ with methanol ($CH_3{}^{13}\underline{C}OOH$ was added as an internal standard to calculate the $H^{13}\underline{C}OO^-$ concentration; reaction conditions: 0.1 mol/L CH_3OH, 1 mol/L $NaH^{13}\underline{C}O_3$, 50% water filling, 50 mg $Pd_{0.5}Cu_{0.5}/C$, 180 °C, and 16 h).

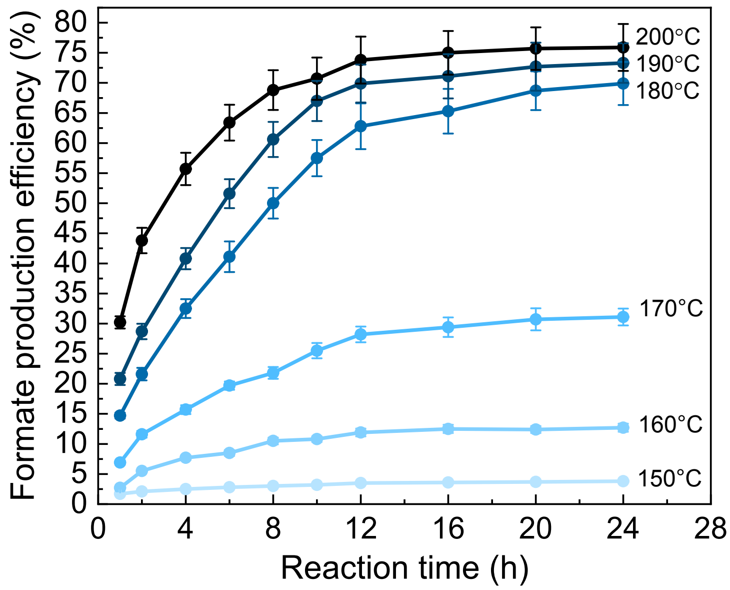

Fig. S7 Effect of reaction temperature and time on the formate production efficiency (reaction conditions: 0.1 mol/L CH_3OH, 1 mol/L $NaHCO_3$, 50% water filling, 50 mg $Pd_{0.5}Cu_{0.5}/C$).

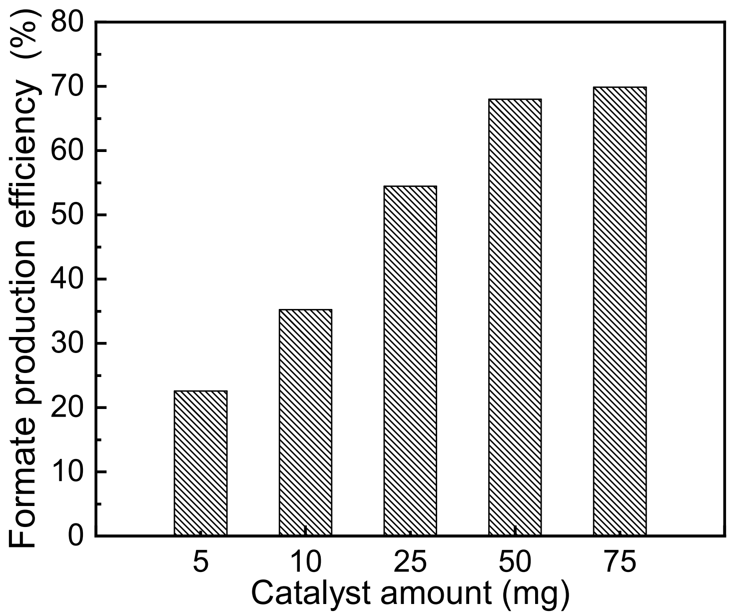

Fig. S8 Effect of catalyst amount on the formate production efficiency (reaction conditions: 0.1 mol/L CH_3OH, 1 mol/L $NaHCO_3$, 50% water filling, 180 °C, 16 h).

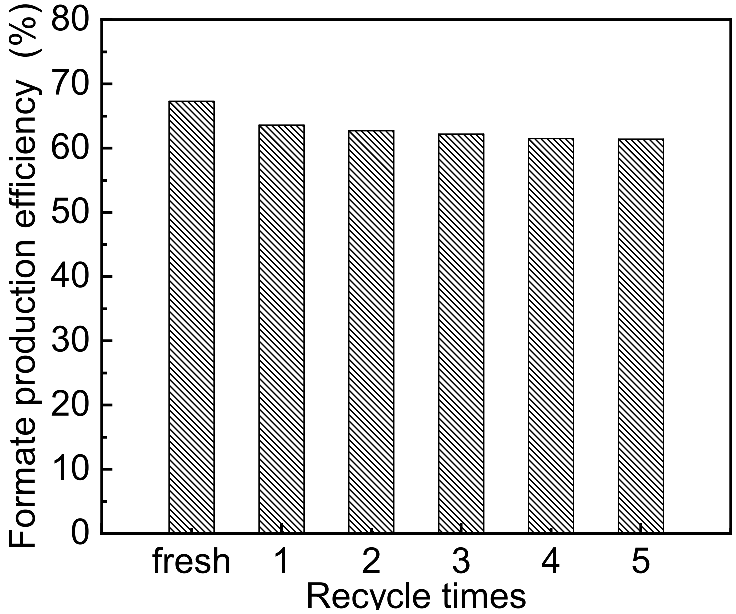

Fig. S9 Recycling test for the stability of $Pd_{0.5}Cu_{0.5}/C$ catalyst (reaction conditions: 0.1 mol/L CH_3OH, 1 mol/L $NaHCO_3$, 50% water filling, 50 mg $Pd_{0.5}Cu_{0.5}/C$, 180 °C, and 16 h).

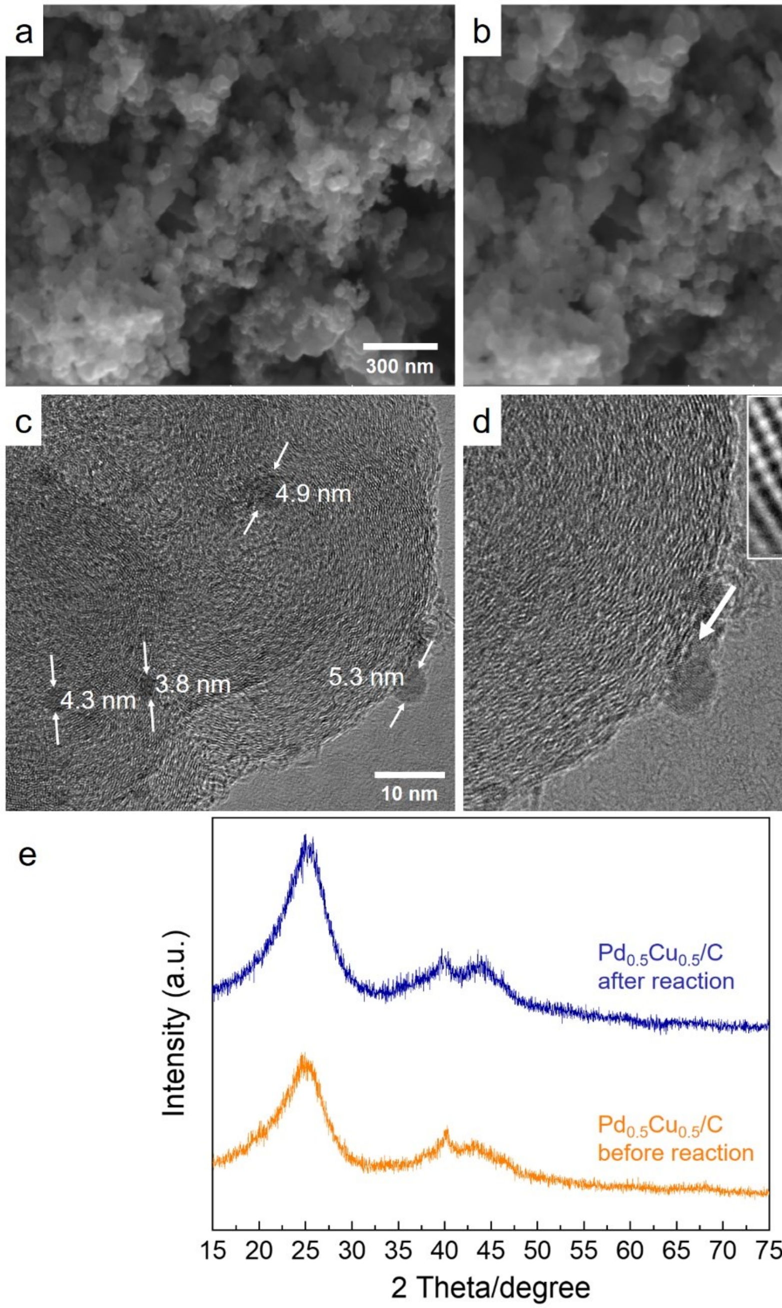

Fig. S10 SEM images (a, b), HRTEM images (c, d) and XRD spetra (e) of the $Pd_{0.5}Cu_{0.5}/C$ catalyst after reaction (reaction conditions: 0.1 mol/L CH_3OH, 1 mol/L $NaHCO_3$, 50% water filling, 50 mg $Pd_{0.5}Cu_{0.5}/C$, 180 °C, and 16 h).

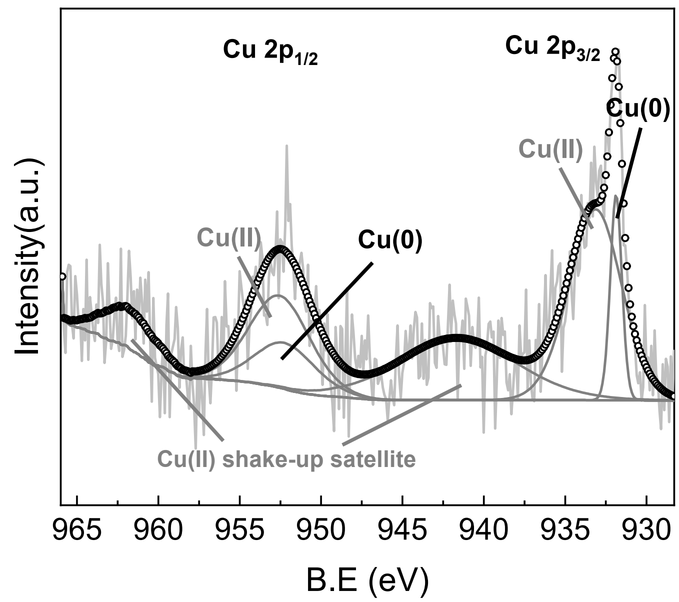

Fig. S11 XPS analyses of Cu 2p in PdCu alloy (a shoulder peak at 932.1 eV and 933.5 eV are observed, which are assigned to Cu(0) and Cu(II) in PdCu alloy, respectively[S2, S3]).

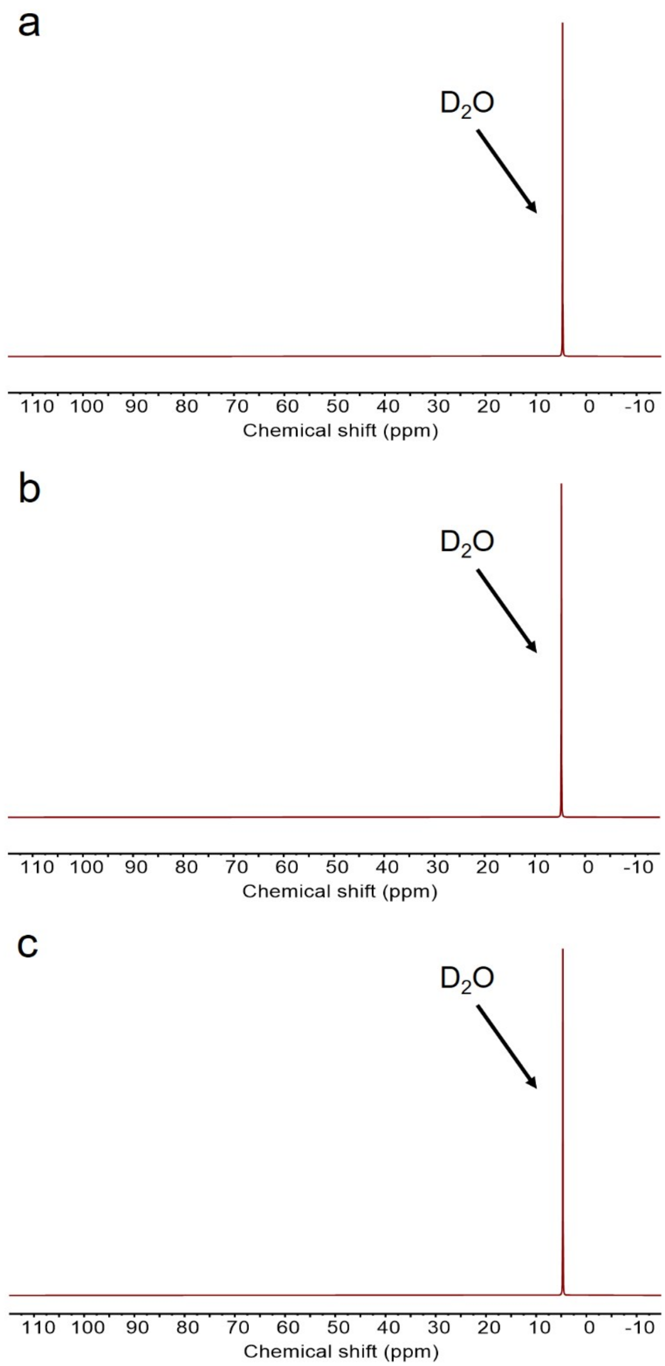

Fig. S12 D-qNMR of the liquid sample after CH_3OH (a), HCHO (b), and $HCOO^-$ (c) reacting with D_2O (reaction conditions: 0.1 mol/L reactant, 50% D_2O filling, 50 mg $Pd_{0.5}Cu_{0.5}/C$, 180 °C, and 16 h).

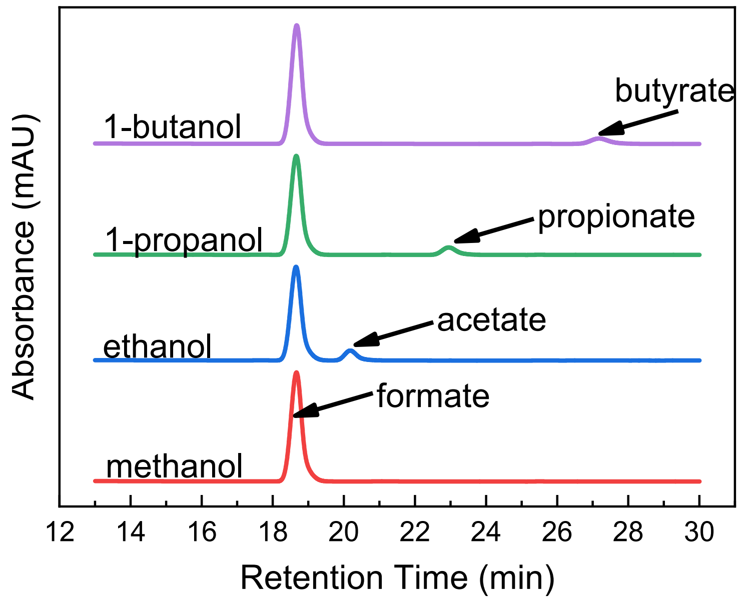

Fig. S13 HPLC spectra of $NaHCO_3$ reduction with different alcohols (reaction conditions: 0.1 mol/L alcohol, 1 mol/L $NaHCO_3$, 50% water filling, 50 mg $Pd_{0.5}Cu_{0.5}/C$, 180 °C, and 16 h).

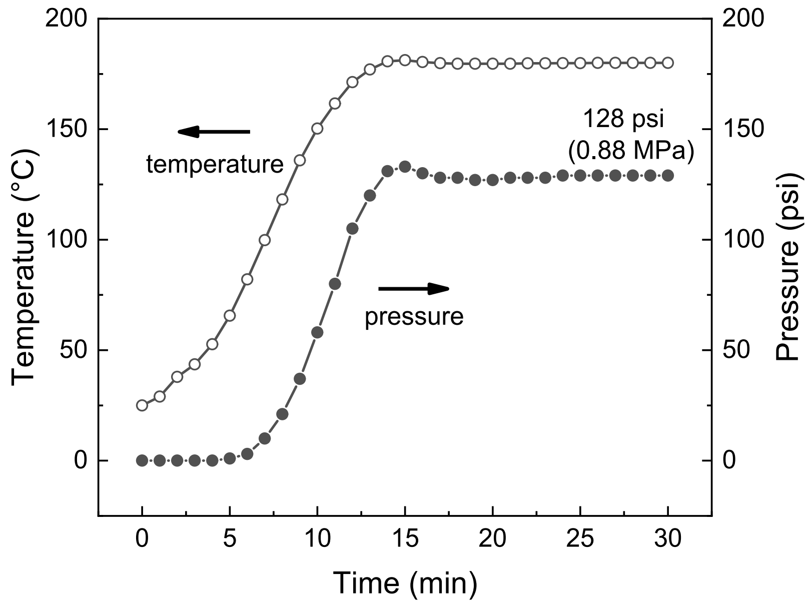

Fig. S14 Variation of the system pressure with reaction time (reaction conditions: 0.1 mol/L CH_3OH, 1 mol/L $NaHCO_3$, 50% water filling and 0.5 g $Pd_{0.5}Cu_{0.5}/C$ in 100 mL PARR reactor).

Table S1 ICP-OES results of the catalysts with different Pd/Cu ratios.

Entry	Catalyst*	wt.%		molar ratio of Pd/Cu
		Pd	Cu	
1	$Pd_{0.75}Cu_{0.25}/C$	6.09	1.17	3.11
2	$Pd_{0.66}Cu_{0.33}/C$	5.54	1.60	2.07
3	$Pd_{0.5}Cu_{0.5}/C$	4.46	2.68	0.98
4	$Pd_{0.33}Cu_{0.66}/C$	3.21	4.07	0.47
5	$Pd_{0.25}Cu_{0.75}/C$	2.44	4.67	0.31

*The subscripted decimal represents the molar fraction of specific metal catalyst to the total metals.

Table S2 Formate yields obtained from the reduction of $NaHCO_3$ with H_2 on different catalysts.

Catalyst	Formate yield (%)
None	None
Pd/C	37.7
Cu/C	12.4
$Pd_{0.5}Cu_{0.5}$/C	49.5

Reaction conditions: 3 MPa H_2, 1 mol/L $NaHCO_3$, 50% water filling, 50 mg catalyst, 180 °C, and 16 h.

References

S1. Y. Yang, H. Zhong, R. He, X. Wang, J. Cheng, G. Yao and F. Jin, Green Chem., 2019, 21, 1247-1252.
S2. J. He, D. Chen, N. Li, Q. Xu, H. Li, J. He and J. Lu, Appl. Catal. B, 2020, 265, 118560.
S3. M. Rahaman, K. Kiran, I. Z. Montiel, V. Grozovski, A. Dutta and P. Broekmann, Green Chem., 2020.