Supplementary information

CO-Free Selective Hydrogenation of CO_2 to Value-Added Formate under Low-Temperature Aqueous Conditions Using a Heterogenized Ru-PNP Catalyst

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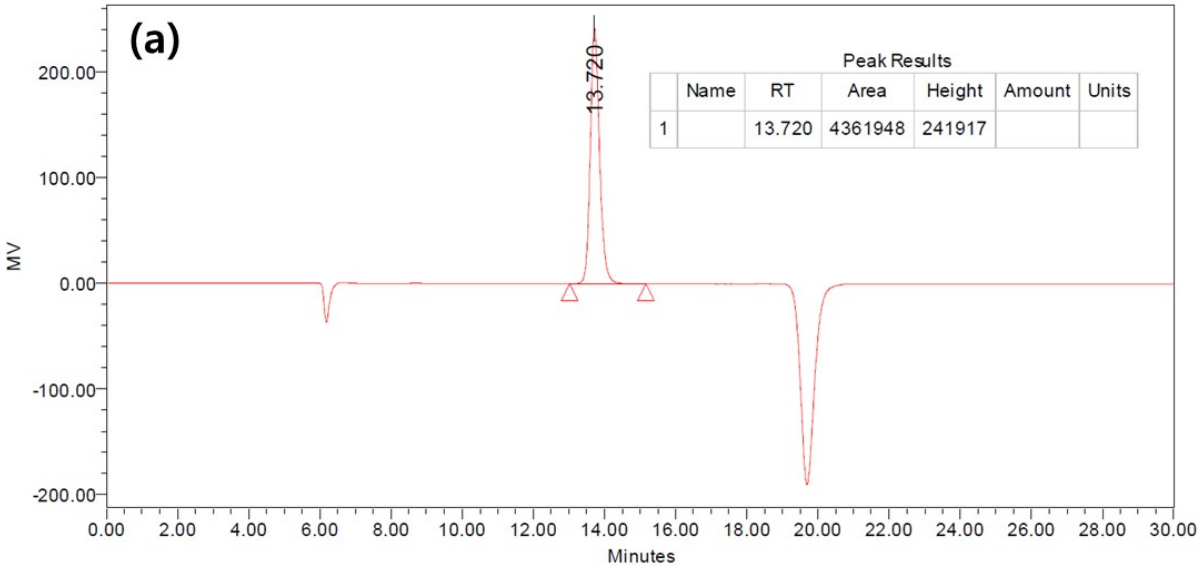
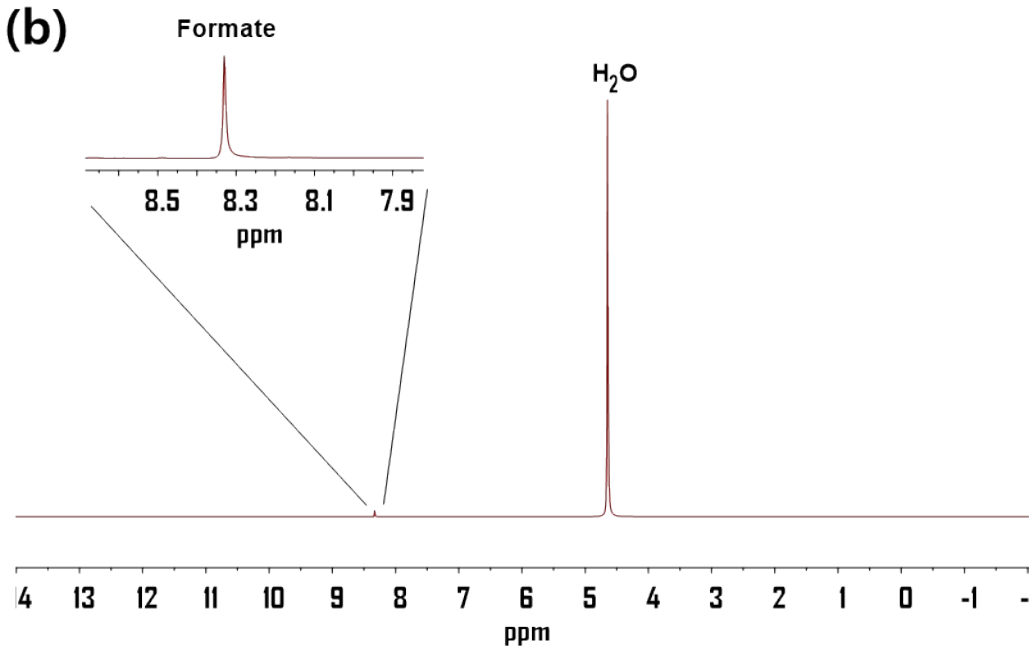
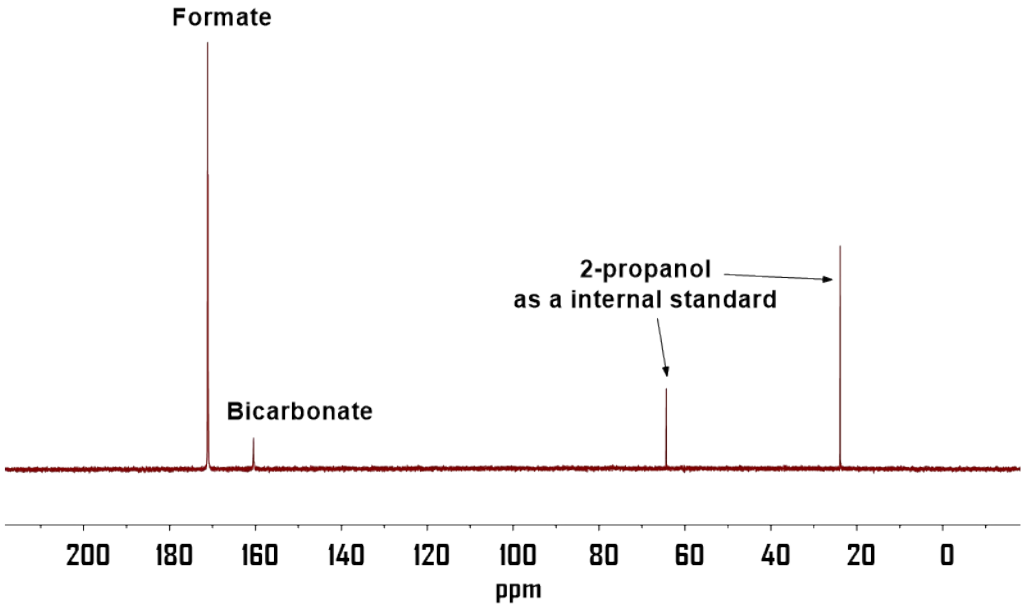
Contents

Figure S1. Representative (a) HPLC, (b) & (C) ^{1}H & ^{13}C NMR spectra (d) GC chromatogram of the potassium formate (HCO_2K) produced after CO_2 hydrogenation.





(c)


Formate
2-propanol
as a internal standard
Bicarbonate
200
180
160
140
120
100
80
60
40
20
0
ppm

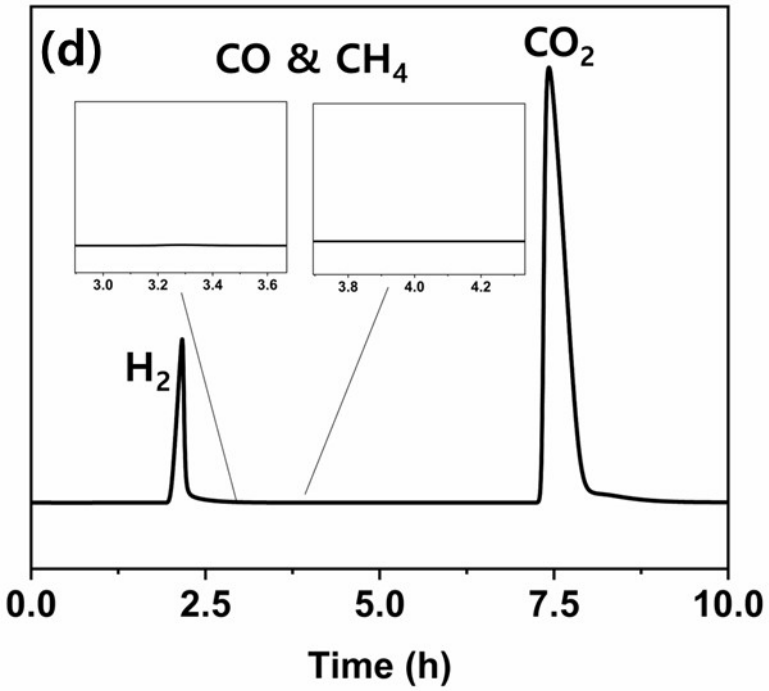

(d)
CO & CH4
CO2
3.0
3.2
3.4
3.6
3.8
4.0
4.2
H2
0.0
2.5
5.0
7.5
10.0
Time (h)

Figure S2. (a) Stainless-steel reactor employed for CO_2 hydrogenation. (b) Overall setup of the hydrogenation system using aqueous KOH, (c) Schematic illustration of the heterogeneous catalyst recycling procedure.

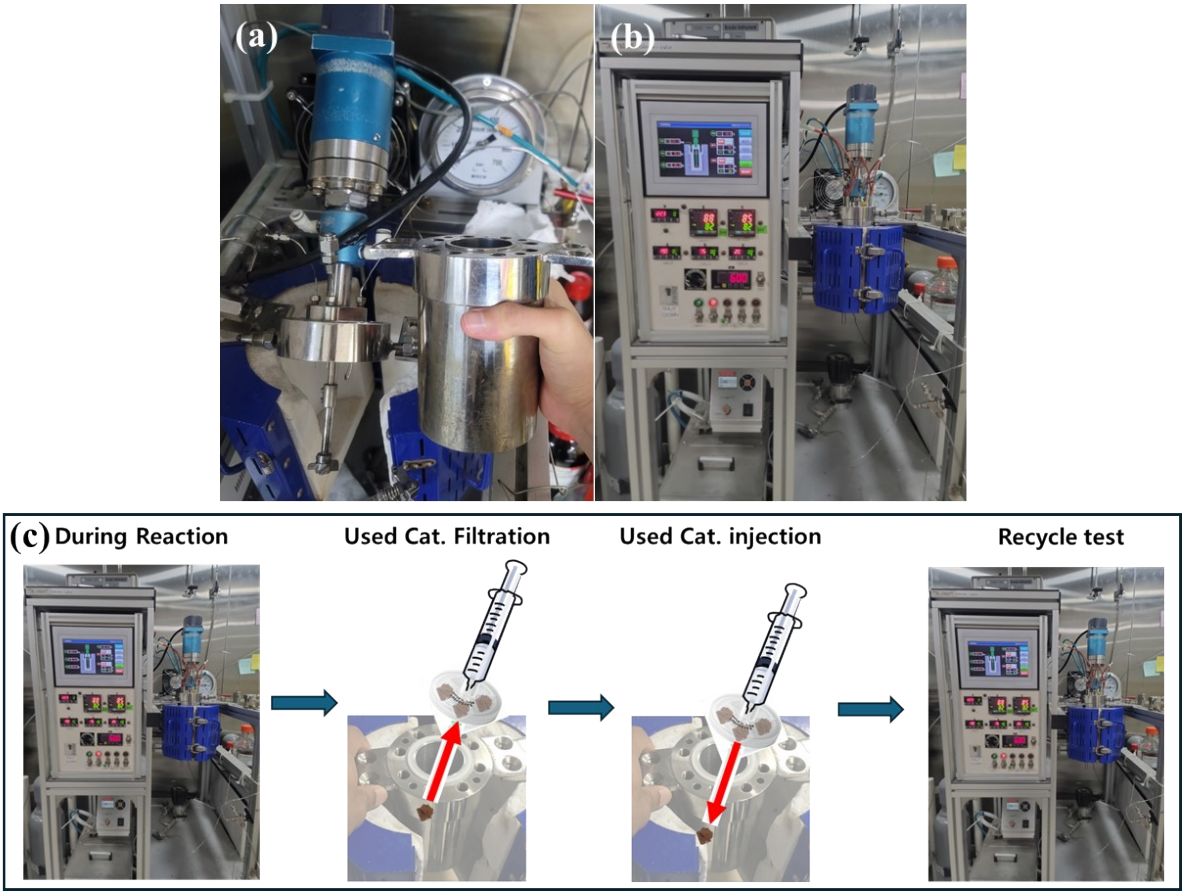
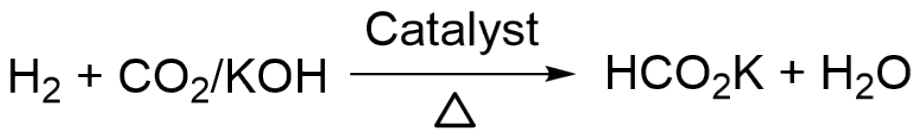


Table S1. Comparison of catalytic performance in KOH-mediated CO_2 hydrogenation.



Entry	Catalyst (cat.)	T (°C)	Time (h)	Yield (%)
1	RuNP@AC	80	16	2.8
2	$RuCl_3$@TN_{20} Bpy_1-CTF	80	16	21
3	$RuCl_3$@DPPE-POP	80	16	29
4	Ru-MACHO-POMP	120	0.5	82
5	Ru-MACHO-POMP	80	2	31
6	Ru-MACHO-POMP	80	16	>99

Table S2. List of abbreviations.

Abbreviation	Full description
KOH	Potassium hydroxide
H_2	Hydrogen
CO_2	Carbon dioxide
CO	Carbon monoxide
CH_4	Methane
Ru	Ruthenium
NN	All types of N,N-bidentate ligands
PP	All types of P,P-bidentate ligands
PNP	All types of tridentate ligands with a P–N–P sequence
POMP	Porous organometallic polymer
Ru-MACHO-POMP	A heterogeneous catalyst synthesized using the Ru-MACHO homogeneous PNP-based catalyst
RuNP@AC	Ru nanoparticles supported on activated carbon
CCU	Carbon capture and utilization
CCS	Carbon capture and storage
DACU	Direct Air Capture and Utilization
K_2CO_3	Potassium carbonate
HCO_2K	Potassium formate
C1 & C2	C1/C2 compounds: Molecules containing one or two carbon atoms
NMR	Nuclear magnetic resonance
ICP-OES	Inductively coupled plasma optical emission spectroscopy