Supporting Information

for

Eco-friendly Upconversion of Limestone into Value-added Calcium Formate

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Figure S1. Schematic representation for the importance of heterogeneous catalyst for the practical realization of CF synthesis.

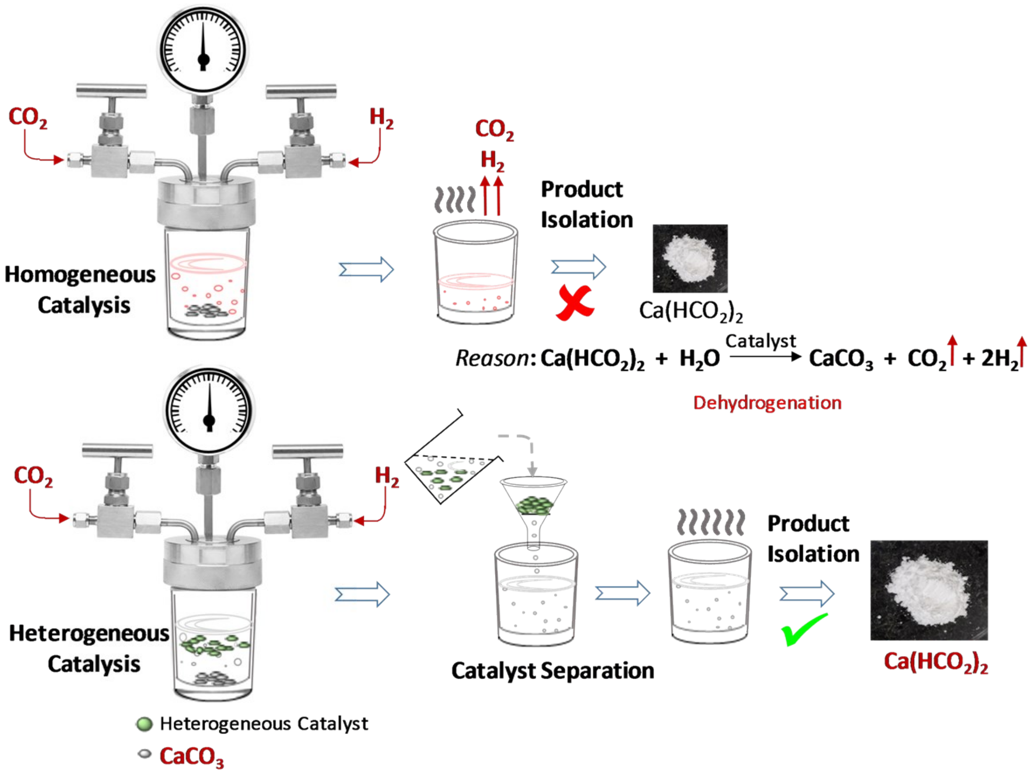


Figure S2. SEM measurement

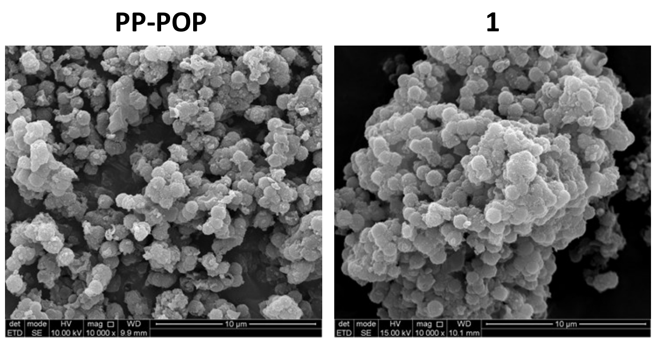


Figure S3. STEM image and mapping of **1**

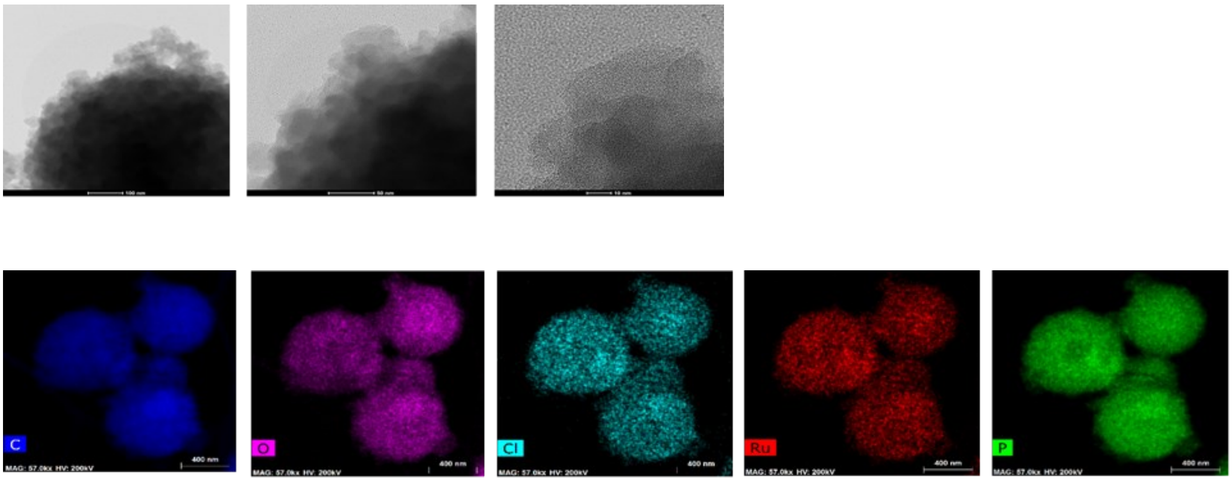


Figure S4. N_2 sorption measurement of PP-POP

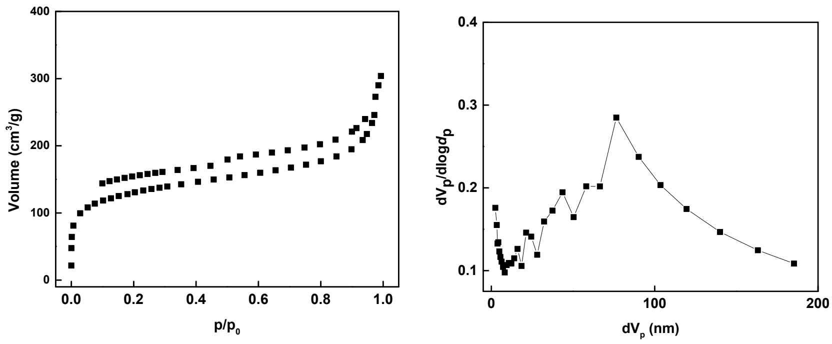


Figure S5. EPR of **1**

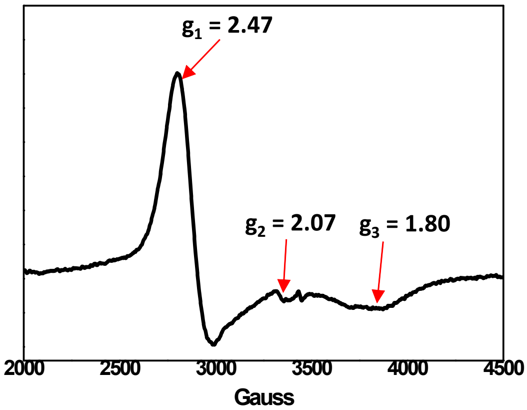


Figure S6. ^{1}H and ^{13}C NMR of reaction mixture (Table 2, entry 1)

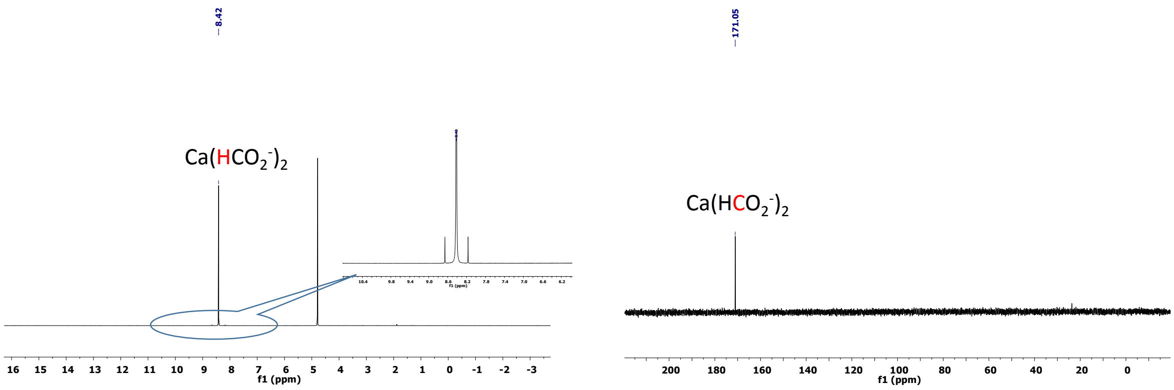
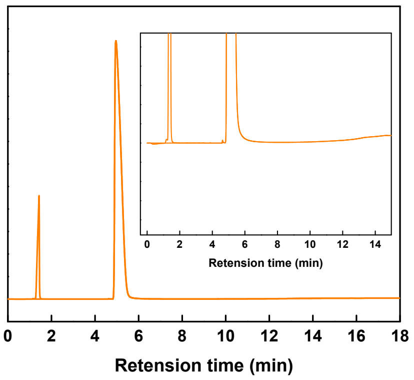


Figure S7. Gas Chromatography results



Gas	Retention Time (min)
H_2	1.40
CH_4	3.20
CO	3.86
CO_2	4.86

Figure S8. ^{1}H and ^{13}C NMR of isolated CF

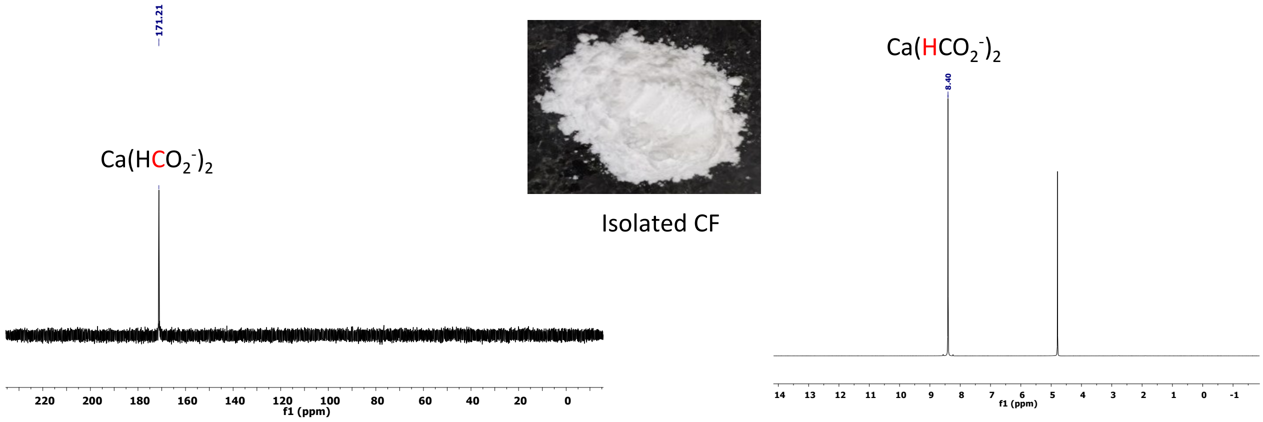


Figure S9. Filtration test results

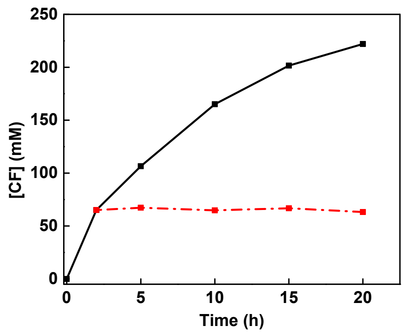


Figure S10. Recyclability of **1**

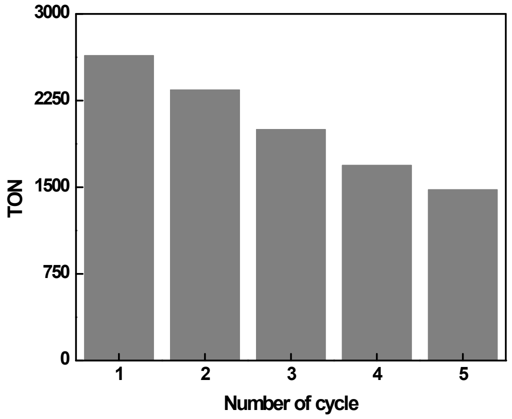


Figure S11. SEM image and STEM-EDS mapping of recovered catalyst

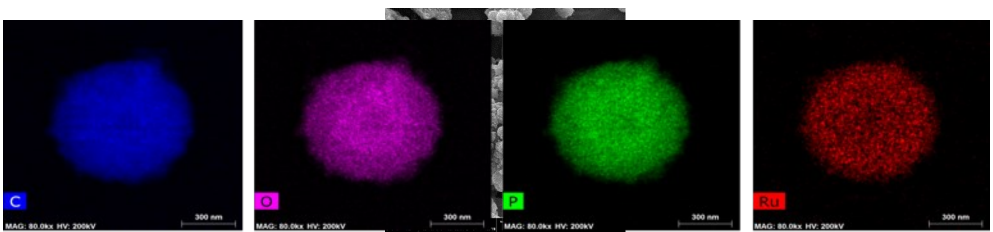


Figure S12. XPS of recovered catalyst

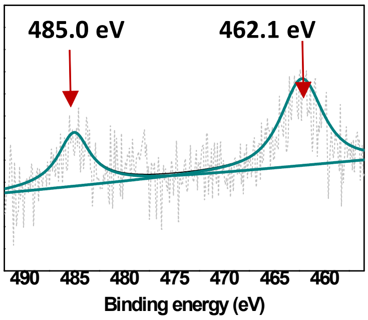
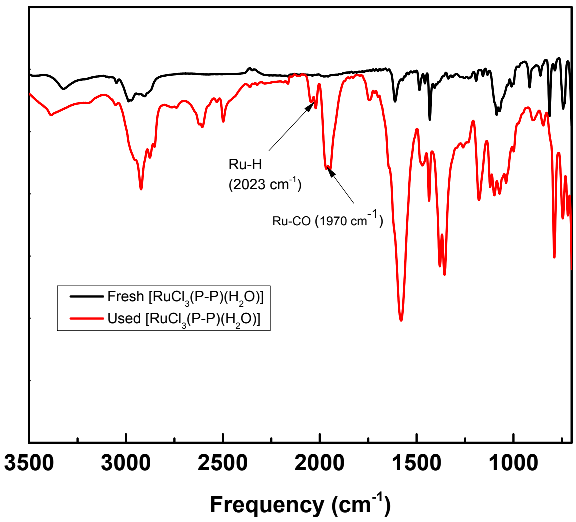


Figure S13. IR of homogeneous [$RuCl_3$(P-P)(H_2O)]



The presence of a new peak at 2023 cm^{-1} indicates the generation of Ru-H intermediate.

The peak at 1970 cm^{-1} corresponds to Ru-CO species, which might have been arising through decarbonylation/dehydration of formate. The similar observation was previously reported by Palkovits *et. al*.[1]

Table S1. Catalytic activity of $[RuCl_3(P\text{-}P)(H_2O)]$ compared with Ferenc Joo's catalysts

Catalyst	Ligand/ Ru	T (°C)	P (MPa)	time (h)	TON	Ref.
$[RuCl_3(P\text{-}P)(H_2O)]$	1	60	6	15	800	This work
$[RhCl(tppms)_3]$	4.5	50	1	15	40	2
$[RhCl(tppms)_3]$	4.5	60	1	15	32	2
$[RhCl(tppms)_3]$	4.5	70	1	15	23	2
$[RhCl(tppms)_3]$	4.5	50	1	15	300	2
$[RhCl(tppms)_3]$	6	24	8	14	262	3
$[RuCl_2(pta)_4]$	4	24	8	14	35	3
$[RuCl_2(tppms)_2]_2$	5	24	8	14	372	3

Table S2. Atomic composition of **1** by SEM-EDX analysis

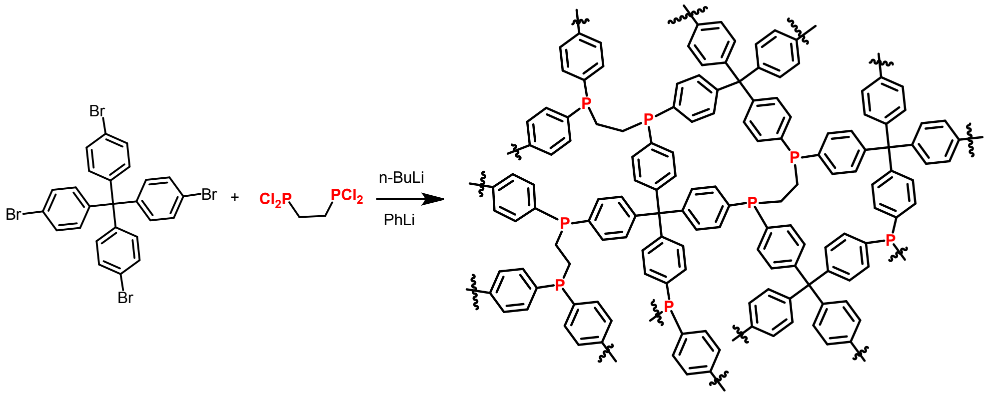
C	O	P	Ru	Cl
82.87	7.04	8.15	0.50	1.44

Table S3. Results of CO chemisorption

Catalyst	Surface atoms by CO chemisorption method
Pd/C	6.9
Ru/Al_2O_3	3.5

Table S4. Atomic composition of recovered catalyst by SEM-EDX analysis

C	O	P	Ru	Cl	Ca
85.32	8.34	5.45	0.45	0.04	0.4



Scheme S1. Synthesis of PP-POP

References:

1. R. Sun, A. Kann, H. Hartmann, A. Besmehn, P. J. C., Hausoul, R. Palkovits, ChemSusChem, 2019, ***12***, 3278 –3285.

2. I. Joszai, F. Joo, *J. Mol. Catal. A Chem*., 2004, ***224***, 87–91.

3. F. Joo, G. Laurenczy, L. Nadasdi, J. Elek, *Chem. Commun*., 1999, 971–972.