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

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Although CaCO<sub>3</sub> is a naturally available, inexpensive, abundant and extensively used chemical in various industries, to date, most of its conversions liberate CO<sub>2</sub> into the atmosphere, which counted about 5 - 6% of global anthropogenic CO<sub>2</sub> emission. Herein, the first synthesis of calcium formate (CF) by hydrogenation of an aqueous mixture of CaCO<sub>3</sub> and CO<sub>2</sub> using a heterogeneous catalyst in the unconventionally CO<sub>2</sub> reducing manner is reported. The phosphine-based heterogenized Ru catalyst efficiently converts CaCO<sub>3</sub> into CF with good selectivity (>99%) and is readily separated from the reaction product, resulting in promising recycling ability. Thus, this work provides a promising strategy for the design of

carbonate

of

## Introduction

Elevated and rapidly rising atmospheric levels of  $CO_2$  constitute a serious threat to the global environment. The most important anthropogenic emission sources of  $CO_2$  are the burning of fossil fuels and chemical processes that release  $CO_2$  as a by-product.<sup>1,2</sup> Thus, it becomes an inevitable target for the chemical industry to develop green and sustainable chemical processes that reduce  $CO_2$  emission, utilize  $CO_2$  as a feedstock, eliminate the use of harsh reaction conditions and toxic compounds, minimize waste, and increase efficiency.<sup>3,4</sup> As such, many syntheses have been accomplished via routes that reduce  $CO_2$  emission and utilize sustainable feedstock, including the synthesis of methanol by  $CO_2$  hydrogenation, the synthesis of furfuryl alcohol via furfural hydrogenation, and transfer hydrogenation of various organic compounds.<sup>5-12</sup>

green

and

sustainable

conversion

Nevertheless, one of the key syntheses that scarcely considered in this platform is the production of calcium formate (CF). CF is a widely used compound in various industries, such as a tanning auxiliary in the leather industry, setting accelerator in the cement industry, deicing agent for roads and airport runways, ensiling agent for silage treatment, desulfurization agent in flue-gases and nutritive supplement in animal feeds.<sup>13-18</sup> Its global production exceeds 100,000 tons/year, which is anticipated to gain increased momentum owing to its promising abilities to generate many C1 potential

chemicals. It is currently synthesized from limestone, i.e. CaCO<sub>3</sub> (from calcite and dolomite minerals) via a two-step process, starting with calcination of CaCO<sub>3</sub> to CaO/Ca(OH)<sub>2</sub> and CO<sub>2</sub>, followed either by a Cannizzaro reaction or carbonylation (Figure 1a).<sup>13-18</sup> However, this process liberates a stoichiometric amount of CO<sub>2</sub> as a by-product (emitting about 160,000 tons of CO<sub>2</sub>eq per year), requires extremely high temperatures (800–1000 °C), and necessitates the use of toxic CO. Thus, the development of CO<sub>2</sub> emission-free and low-temperature synthetic pathway is undoubtedly essential for CF synthesis.

minerals

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#### (a) Current Industrial CO<sub>2</sub> Emission Method

$$CaCO_{3} \xrightarrow{\sim 1000 \ ^{\circ}C} CaO + CO_{2} \uparrow$$

$$H_{2}O \downarrow \qquad (Emission ≈ 160,000 \text{ tons/yr})$$

$$Ca(OH)_{2} \xrightarrow{2CO} Ca(HCO_{2})_{2}$$

$$\downarrow R-CHO$$

$$Ca(HCO_{2})_{2} + R-CH_{2}OH$$

(b) Eco-friendly method (This Study)

$$CaCO_3 + CO_2 + 2H_2 \xrightarrow{I} Ca(HCO_2)_2 + H_2O$$
  
(Utilization)

**Figure 1**. Routes to synthesize calcium formate: (a) current industrial method; (b) eco-friendly CO<sub>2</sub> utilization method.

One of the ideal, economical, and eco-friendly methods to synthesize CF would be the hydrogenation of an aqueous mixture of  $CaCO_3$  and  $CO_2$  (Figure 1b), which presents many advantages. First,  $CaCO_3$  is inexpensive and abundant and thus provides an affordable means to  $CO_2$  utilization. Second, the use of water as a reaction medium enables the synthesis to

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proceed at relatively low temperatures and pressures. Third, the atom economy for the reaction is 100%; thus, no waste is





released. Fourth, toxic CO is not used in the process. Fifth, the use of renewable  $H_2$  renders the entire process sustainable and environmentally friendly. Finally, among various  $CO_2$  emission conversions of CaCO<sub>3</sub>, this transformation utilize its carbon content and additional  $CO_2$  to prepare value-added chemical. Nevertheless, the synthesis of CF through this method was not realized and yet on a proposal level.

To the best of our knowledge, only a couple of reports, by Ferenc Joo, attempted the synthesis of CF through this method a long time ago, where Ru- and Rh-based organometallic complexes with excess monophosphine ligands were used as homogeneous catalysts.<sup>19,20</sup> However, those catalysts are inactive or less active in the absence of excess ligands, and thus the role of additional ligands is unclear. In addition, the efficiency of these catalysts is significantly low; a maximum turnover number (TON) of 372 was obtained. These obstacles restrict the understanding of mechanistic pathway and the design of efficient catalysts for practical realization.



Figure 2. Realizing the CF synthesis through heterogeneous catalysis.

To overcome these drawbacks, we envisioned to use a well-defined bidentate bisphosphine complex  $[RuCl_3(P-P)(H_2O)]$  (P-P = 1,4-bis(diphenylphosphino)butane, Scheme 1a) for this hydrogenation. As shown in table S1, entry 1, the complex successfully generated CF from CaCO<sub>3</sub> over CO<sub>2</sub> pressure with a concentration of 144.0 mM and a TON of 800

at relatively mild reaction conditions (60 °C, 6 MPa, 15 h). Notably, this value is almost double to that of Ferenc Joo's catalysts,<sup>19,20</sup> and the catalyst does not require any excess additional ligands. Nevertheless, the isolation of the generated formate from the homogeneous catalytic medium was commonly infeasible owing to their efficient promotion of the reverse reaction namely dehydrogenation of formate back into (bi)carbonate/CO<sub>2</sub> and H<sub>2</sub> during product separation step (Figure S1).<sup>21,22</sup>

Therefore, to realize this eco-friendly synthesis of CF in industry, the use of heterogeneous/heterogenized catalysts is highly desirable as they can be easily separated from the reaction medium prior to product isolation and can be continuously recycled for successive runs with trivial operations (Figure 2). In this context, no such dedicated efforts have been undertaken and this is the first attempt to tailor a heterogeneous catalyst for this hydrogenation. Upon designing a heterogeneous counterpart of [RuCl<sub>3</sub>(P-P)(H<sub>2</sub>O)], we envisaged that catalyst constructed with modern catalytic supports, such as solid organic functional ligands, might exhibit enhanced and promising catalytic performance owing to the electron-donating ability and highly dispersive character of the matrices.<sup>23-25</sup> In addition, hydrogenation in fixed bed reactors may be infeasible in the industry because CaCO<sub>3</sub> is insoluble, and thus, the hydrogenation process may necessitate slurrytype reactors, such as fluidized bed reactors. With these understandings, herein, we first report the synthesis of CF by hydrogenation of an aqueous mixture of CaCO<sub>3</sub> and CO<sub>2</sub> using a specially tailored phosphine-based heterogenized Ru catalyst (1) (Scheme 1b). The catalyst is efficient towards CF production and showed a maximum TON of 2800 with good recycling ability. In addition, the plausible mechanistic pathway is proposed for future designing and understanding. Most importantly, the catalyst was separated from the reaction medium by filtration, and the generated CF in the filtrate was isolated in a very pure form upon evaporation of the solvent, H<sub>2</sub>O.

## **Results and discussion**



Figure 3. Characterization of 1. (a) STEM image (scale bar = 400 nm); (b) EDX mapping of the Ru atoms; (c)  $N_2$  sorption measurement; (d) Deconvoluted X-ray photoelectron spectra of Ru-3p core level.

The synthetic route for the preparation of 1 is depicted in Scheme 1b. Following a previously developed method,<sup>26</sup> the preparation of PP-POP was achieved through tetra-fold lithiation of tetrakis(4-bromophenyl)methane, followed by subsequent cross-linking with 1.2bis(dichlorophosphino)ethane and capping with phenyllithium. The distinct phosphine sites of PP-POP can serve as a potential solid chelating ligand to coordinate a Ru cation. Metalation of PP-POP with RuCl<sub>3</sub>.xH<sub>2</sub>O was conducted by reacting PP-POP with  $RuCl_3$  in a refluxing methanol solution under an atmosphere of N<sub>2</sub> to obtain a fine ivory color precipitate of 1 (Scheme 1b). Inductively coupled optical emission spectrometry (ICP-OES) analysis indicated that approximately 0.81 wt% of Ru was incorporated into PP-POP. Scanning electron microscopy (SEM) analysis showed that the original morphology and particle size were unaltered upon Ru coordination (Figure S2). Scanning transmission electron microscopy (STEM) measurements confirmed the uniform binding of Ru cations onto PP-POP with a 1:3 ratio of Ru to Cl (Figure 3a-b and S3, Table S2). N<sub>2</sub> sorption measurement of 1 revealed an adsorption isotherm similar to that of PP-POP, with a BET surface area of 469 m<sup>2</sup>g<sup>-1</sup> and a total pore volume of 0.475 cm<sup>3</sup>g<sup>-1</sup> (Figures 3c and S4). These hierarchical pores in 1 could gently expose the Ru sites to reactants and help to improve the catalytic process. X-ray photoelectron spectroscopic (XPS) measurements reveal that the binding energy of Ru for Ru- $3p_{3/2}$  level is 462.2 eV, which indicates the +3 valence state of Ru in 1 (Figure 3d).27 Notably, the high binding energy of Ru compared to Ru precursor  $RuCl_3$  (Ru-3 $p_{3/2}$ = 463.5 eV) clearly indicates the donation of electron density from the bidentate phosphine ligands to the Ru site and successful complexation of Ru with PP-POP as depicted in scheme 1b. Electron paramagnetic resonance (EPR) analysis showed that **1** is low-spin  $d^5$  complex with g values of 2.47,

2.07 and 1.80, reiterating the +3 valence state of Ru (Figure S5). Ru(3+) coordination compounds with diphosphine ligands, such as 1,4-Bis(diphenylphosphino)butane, have been reported and their oxidation states were determined using the EPR analysis with anisotropic g values in a range similar to these of  $1.^{28-31}$ 

The hydrogenation of an aqueous mixture of CO<sub>2</sub> with soluble bases (such as NaOH, KOH, NaHCO<sub>3</sub>, KHCO<sub>3</sub>, NH<sub>4</sub>HCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and Et<sub>3</sub>N) has been extensively investigated over the past three decades, and many highly active heterogeneous catalytic entities were developed.<sup>32-41</sup> However, upon applying these catalysts to this insoluble CaCO<sub>3</sub> substrate, only a very low amount of CF has been generated (Table 1). For instance, the well-known Pd on carbon (Pd/C) generated a [CF] of 7.5 mM. The half-sandwich Ir and Ru based catalysts produced a maximum [CF] of 23.2 mM. Similarly, the simple RuCl<sub>3</sub> immobilized catalyst generated a [CF] of 44.6 mM. These results undoubtedly indicate that a novel and efficient catalytic system for this insoluble CaCO<sub>3</sub> substrate is imperative. Hence, here we utilized a bisphosphine-based Ru catalyst (1) for this CaCO<sub>3</sub> hydrogenation, which generated a very high [CF] of 148.5 mM with a TON of 550 under identical reaction conditions (Table 1).

Table 1. Catalyst screening for the hydrogenation of aqueous mixtures of CaCO\_3 and  $\text{CO}_2{}^a$ 

Catalyst	[CF] (mM)	TON⁵
Pd/C	7.5	95 (1350)°
$Ru/Al_2O_3$	3.5	44 (1250) <sup>c</sup>
IrCp*@bpy-CT	F 23.2	290
Ru(C <sub>6</sub> Me <sub>6</sub> )@bpy-	CTF 18.1	225
IrCp*@bpy-CT	F 13.7	170
RuCl₃@bpy-CT	F 44.6	550
IrCl₃@bpy-CTF	38.4	480
RuCl₃@PP-POF	P 148.5	1850

<sup>a</sup>Reaction conditions: 1.0 g of CaCO<sub>3</sub> in 20 mL water with catalyst [M] = 0.08 mM, temperature = 80 °C, time = 20 h, total pressure at room temperature = 8 MPa [ $p(CO_2)/p(H_2) = 1$ ]. <sup>b</sup>TON = total moles of CF formed/total moles of metal. <sup>c</sup>TON = total moles of CF formed/(total moles of metal × metal dispersion). Metal dispersion values were calculated from CO chemisorption (Table S3).

In this regard, the catalytic ability of **1** towards CF synthesis was screened under various reaction conditions to achieve an optimal condition. Initially, the catalyst was screened at 120 °C and 2 MPa total pressure (with an equal ratio of  $H_2/CO_2$ ) for 20 h with 1.0 g CaCO<sub>3</sub> in 20.0 mL water. As shown in table 2, entry 1, it produced 21.3 mM of CF in 20 h with a TON 260. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy measurements showed that the reaction mixture contains only CF (Figure S6): no other compounds including methanol, formaldehyde, carbonate, and bicarbonate) were observed. Gas chromatography analysis showed almost no detectable generation of CO and CH<sub>4</sub> (Figure S7). These results clearly indicating that the catalyst **1** produces CF with high selectivity. To evaluate the effect of

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reaction temperature, hydrogenation was then carried out at various temperatures ranging 60-120 °C. As shown in table 2, entries 1-5, the equilibrium concentration of CF gradually decreased with increasing temperature, indicating that the reverse reaction is faster at higher temperatures. Next, the pressure dependence of the catalytic activity of 1 was examined from 2 to 8 MPa at 60 °C. From table 2, entries 5-8, it is evident that the equilibrium concentration of CF shifts toward the product side at higher pressure. The catalyst showed a maximum of a TON of 2800 under 8 MPa total pressure, which is by far the highest number achieved in this hydrogenation. We anticipate the following reasons for the high activity of catalyst 1 compared to these of other catalysts in Table 1. A) High electron donating ability of phosphine ligands: Theoretical investigations on CO<sub>2</sub> hydrogenation demonstrated that the ligands which improve the electron density on central metal ions would enhance the efficiency of this catalytic reaction.<sup>42</sup> In this regard, the high electron donating ability of phosphine ligands might have enhanced the electron density on central metal ions and thus showed higher catalytic ability. B) High dispersive character: The high dispersive character of 1 in the reaction medium might have improved its interaction with the substrate molecules (CaCO<sub>3</sub>, CO2 and H2) and thus reduce the mass transfer problems, which consequently enhanced the activity of 1. Notably, upon performing the hydrogenation in the absence of CO<sub>2</sub> pressure the catalyst showed a very low TON (table 2, entry 9); which indicates that while applying CO<sub>2</sub> pressure the solution gets acidified, leading to the formation of water-soluble Ca(HCO<sub>3</sub>)<sub>2</sub>,<sup>43</sup> which might be the active substrate for the hydrogenation catalyzed by 1.

Table 2. Hydrogenation of aqueous mixtures of CaCO<sub>3</sub> and CO<sub>2</sub> using  $\mathbf{1}^a$ 

Entry	т (°С)	Р	[CF] (mM)	TON <sup>c</sup>	
		(MPa) <sup>ь</sup>			
1	120	2	21.3	260	
2	100	2	36.0	450	
3	90	2	52.6	650	
4	70	2	81.1	1000	
5	60	2	128.4	1600	
6	60	4	140.4	1750	
7	60	6	184.1	2300	
8	60	8	222.3	2800	
9 <sup>d</sup>	60	4	15.2	200	

<sup>a</sup>Reaction conditions: 20.0 mg of **1** in 20 mL of water with 1.0 g of CaCO<sub>3</sub>, time = 20 h. <sup>b</sup>Total pressure at room temperature with  $p(CO_2)/p(H_2) = 1$ . <sup>c</sup>TON = total moles of CF formed/total moles of metal. <sup>d</sup> $p(CO_2) = 0$ ;  $p(H_2) = 4$  MPa.

An important goal of this study is to separate the catalyst from the reaction medium and isolate the generated CF. Therefore, the catalyst after the first run was separated from the reaction medium via simple filtration and washed with water. The filtrate was then completely evaporated, dried in a vacuum oven at 120 °C to obtain white solid of CF with about >98% yield (Figure S8). The <sup>1</sup>H and <sup>13</sup>C NMR analyses showed that the obtained CF is very pure and free-from any (bi)carbonate salts (Figure S8). These results indicate that the use of a heterogeneous catalyst enables the synthesis and successful isolation of CF through hydrogenation of CaCO<sub>3</sub>/CO<sub>2</sub> and thus opens the potential of this eco-friendly CF synthetic method in the industry.



Figure 4. Plausible reaction mechanism for the synthesis of CF over 1.

The hot filtration test revealed that the catalyst **1** is purely working in a heterogeneous fashion throughout the reaction (Figure S9). ICP-OES analysis of the filtrate showed that about 1.3% of loaded Ru is leached out into the solution. To check the recyclability of 1, the precipitate obtained after the initial run was used for consecutive runs. As shown in Figure S10, the efficiency of the catalyst is diminished in each runs, which might be attributed to the weight loss upon handling and small leaching of Ru species. SEM analysis of the recovered solid showed that it retained its original morphology (Figure S11). SEM-EDS analysis detected the presence of Ca ions in the sample (Table S4), which might be due to the co-existence of unreacted  $CaCO_3$  as the separation of **1** from this insoluble CaCO<sub>3</sub> was infeasible. In addition, no presence of chlorine was detected in EDS, suggesting that chlorine had no significance in the reaction and was replaced with other ligands (like  $H_2O/hydride/formate or HCO_3^{-})$  during the reaction cycle. As shown in Figure S11, the recovered solid maintains the uniform distribution of Ru species throughout the particle. XPS analysis of the recovered catalyst showed that the original oxidation state of Ru(III) is well-maintained during the hydrogenation (Figure S12). Nevertheless, FT-IR analysis of used homogeneous [RuCl<sub>3</sub>(P-P)(H<sub>2</sub>O)] revealed that it generates CF via Ru-hydride intermediate (Figure S13). Based on these considerations and previous literature on the hydrogenation,44-48 a plausible mechanism for CF synthesis from CaCO<sub>3</sub> is proposed in Figure 4. The mechanistic pathway involves the generation of a Ru-hydride intermediate through the substitution of the Cl ligand with H<sub>2</sub> and H<sub>2</sub>O. Then, the nucleophilic attack of the thus-formed Ru-hydride complex

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with  $Ca(HCO_3)_2$  generates Ru-formate species, which finally releases out from the catalytic cycle through oxidative addition of H<sub>2</sub> and regenerates the Ru-hydride intermediate.

### Conclusions

In summary, we report the first practical synthesis of CF via hydrogenation of an aqueous mixture of  $CaCO_3$  and  $CO_2$  using a heterogeneous catalyst at relatively low temperature (60 °C). The tailored phosphine-based heterogeneous Ru catalyst efficiently converts  $CaCO_3$  into CF with a maximum turnover number of 2,800. The catalyst was reused in consecutive cycles and the generated CF was successfully isolated from the reaction medium. Thus, this work highly significant in realizing  $CO_2$ -emission free conversion of  $CaCO_3$  into value-added chemicals in industry.

## **Experimental section**

#### 4.1 Materials and Characterization

All chemicals purchased were of analytical grade and used without further purification unless otherwise mentioned. The following chemicals were purchased from Sigma Aldrich: 1,2bis(dichlorophosphino)ethane, n-butyllithium (1.6 M in hexanes), phenyllithium (1.8 M in ether), Ruthenium chloride hvdrate were. CaCO<sub>3</sub> and Pd/C. Tetrakis(4bromophenyl)methane was obtained from Tokyo Chemical Industry Co., Ltd. Ru/Al<sub>2</sub>O<sub>3</sub> was purchased from Alfa Aesar Chemicals. CO<sub>2</sub> (99.999%) and H<sub>2</sub> (99.999%) were supplied by Sinyang gas industries. Homogeneous [RuCl<sub>3</sub>(P-P)(H<sub>2</sub>O)],<sup>30</sup> IrCp\*@bpy-CTF,<sup>41</sup> Ru(C<sub>6</sub>Me<sub>6</sub>)@bpy-CTF,<sup>34</sup> IrCp\*@NHC-CTF,<sup>35</sup> RuCl<sub>3</sub>@bpy-CTF,<sup>37</sup> and IrCl<sub>3</sub>@phen-POP,<sup>39</sup> were prepared according to the reported procedure.

The instrument iCAP-Q from Thermo fisher scientific has been used to measure ICP-OES for analyzing the ruthenium content in 1. Prior to ICP-OES analysis, 1 was digested using microwave acid digestion system (MARS6, CEM/U.S.A): 1 (10.0 mg) were digested in a mixture conc. HNO<sub>3</sub> (5.0 mL) solution under microwave rays at 280 °C for 20 min (ramp rate = 25 °C/min). The instrument INSPECT F JEOL LTD from Japan JEM-7610F operated at an accelerating voltage of 20.0 kV was used for the measurement of SEM and EDS. Belsorp II mini, BEL Japan, Inc., was utilized to characterize the porous character of materials through N<sub>2</sub> sorption analysis at 77 K; prior to analysis the samples were degassed at 80 °C for 12 h. A TEM-Talos; F 200X system was used for the STEM measurements. XPS data's were acquired on an ESCA 2000 (VG microtech) at a pressure of ~3 x 10<sup>-9</sup> mbar using Al-Ka as the excitation source (hy=1486.6 eV) with concentric hemispherical analyzer. Solution state <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy were measured on a 400 MHz NMR spectrometer (ASCEND III HD, Bruker, Germany). Waters Alliance 2695 system equipped with a refractive index detector and an Aminex HPX-87H column was utilized for high-performance liquid chromatography (HPLC) to find the concentration of formate; All of the results, including the calibration curve for formic acid detection/quantification,

were obtained at a column temperature of 50 °C and a mobile phase of 5.00 mM  $H_2SO_4$  solution with a flow rate of 0.6 mL/min. The gas mixtures from the hydrogenation reactor was analyzed by Gas chromatography equipped with a Flame ionization and thermal conductivity detectors, Mol Sieve 13X and porapak N columns, and a carrier gas of N<sub>2</sub> (20 mL/min) on YL-6500 instrument (Younglin, Republic of Korea): Calibrations were determined with a gas mixture containing known amounts (100, 1000, 5000 ppm) of CO and CH<sub>4</sub>.

#### Synthesis of PP-POP

The PP-POP was prepared by following a reported procedure (Scheme S1),<sup>26</sup> however with tetrakis(4-bromophenyl)methane as a linker. n-BuLi (0.806 g, 12.580 mmol) was added to a solution of 4,4'-tetrakis(p-bromophenyl)methane (1.062 g, 1.572 mmol) in Et<sub>2</sub>O (30.0 mL) and left to stir inside a glovebox for 1.5 h. The generated white solid was separated through filtration over a glass filter and washed with ether (100 mL) followed by hexane (100 mL). The solid was then suspended in THF (50 mL) and a solution of bis(dichlorophosphino)ethane (0.364 g, 1.572 mmol) in THF (8.0 mL) was added dropwise and the pale pink suspension was stirred at 20 °C for 2 h. Subsequently, phenyllithium (0.125 g, 1.494 mmol) was added and the dark purple suspension left to stir for 24 h. Then, MeOH (50 mL) was added to quench the reaction and left to stir for 10 min. The pale suspension was filtered over a glass filter and repeatedly washed with MeOH (50 mL × 2) followed by Et<sub>2</sub>O (200 mL). The solid was finally dried overnight under vacuum at 60 °C for 16 h. (Yield = 0.582 g).

#### Synthesis of 1

A solution of RuCl<sub>3</sub>.xH<sub>2</sub>O (0.026 g) in 30.0 mL methanol was added to a vigorously stirred suspension of PP-POP (1.00 g) in 60.0 mL methanol. The reaction mixture was stirred at reflux conditions for 48 h. Then, the generated off-white solid was filtered and repeatedly washed with methanol (10.0 mL x 6), and dried under vacuum at 60 °C for 16 h. (Yield = 0.988 g).

#### Representative procedure for the hydrogenation

In the reactor vessel, catalyst **1** (0.02 g) and CaCO<sub>3</sub> (1.00 g) were dispersed in 20.0 mL water, and tightly closed without any leak. The reactor was initially pressurized with  $CO_2$  and then with  $H_2$  (1:1) to the desired pressure at room temperature and heated at 60-120 °C. After the reaction time, the reactor was air cooled and the gases were slowly vented inside a working hood, and the reaction mixture was unloaded from the vessel. The concentration of the CF was analyzed by HPLC. For recycling experiments, the solid was filtered after each run, washed with water (2\*10 mL), and dried under vacuum at 80 °C for 12 h. The obtained solid was then used for the next run.

## **Conflicts of interest**

There are no conflicts to declare.

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## TOC

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



We first report  $CO_2$  emission-free conversion of  $CaCO_3$  into calcium formate (CF) using a heterogeneous catalyst. The designed bisphosphine-based Ru catalyst efficiently produces CF through the hydrogenation of  $CaCO_3$  (TON = 2,800) at relatively low-temperature (60 °C) with good selectivity (99%). The catalyst can be reused and the generated CF can be isolated in a very pure quality.