

## Carbonate-Catalyzed CO<sub>2</sub> Hydrogenation to Multi-Carbon Products

### Investigators

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### Abstract

A grand challenge for the 21<sup>st</sup> century is to drastically reduce greenhouse gas emissions without compromising quality of life for a growing population. Using CO<sub>2</sub> as a feedstock for chemical and material synthesis—a process termed CO<sub>2</sub> utilization—could substantially reduce greenhouse gas emissions by displacing fossil use or creating “carbon negative” products that effectively permanently sequester CO<sub>2</sub>. The ultimate challenge is to develop renewably-powered energy efficient processes that utilize CO<sub>2</sub> for the synthesis of high-volume products. An appealing strategy is to produce H<sub>2</sub> by using renewable energy to electrolyze H<sub>2</sub>O and then synthesize multi-carbon compounds by hydrogenating CO<sub>2</sub>. Renewable H<sub>2</sub> can be produced today using electrolyzers powered by photovoltaics or wind turbines, albeit at a higher cost than natural gas-derived H<sub>2</sub>; emerging photoelectrochemical technologies may lower the cost in the future. The key obstacle to using renewable H<sub>2</sub> to synthesize multi-carbon compounds is the absence of effective CO<sub>2</sub> hydrogenation methods. Despite decades of research, currently available CO<sub>2</sub> hydrogenation methods are only useful for synthesizing methane, CO, or methanol. All of these methods use metal or metal oxide surfaces as catalysts. The absence of efficient multi-carbon product synthesis in this paradigm is understandable given the enormous challenges of designing a single surface that activates H<sub>2</sub> and CO<sub>2</sub> and mediates C–C bond formation in a controlled manner.

The goal of this project was to evaluate a completely new approach to CO<sub>2</sub> hydrogenation that uses simple alkali carbonate salts (M<sub>2</sub>CO<sub>3</sub>) as catalysts instead of transition metals or metal oxides. The use of carbonate (CO<sub>3</sub><sup>2-</sup>) as a catalyst was inspired by our prior discovery that, in solvent-free organic alkali salts, CO<sub>3</sub><sup>2-</sup> deprotonates unactivated C–H bonds, generating carbanion (C<sup>-</sup>) intermediates that undergo C–C bond-forming reactions with CO<sub>2</sub>. We hypothesized that this “super-basicity” exhibited by CO<sub>3</sub><sup>2-</sup> could be harnessed to activate H<sub>2</sub> in the presence of CO<sub>2</sub>, generating H<sup>-</sup> to initiate CO<sub>2</sub> hydrogenation pathways. The research consisted of experimental studies in the Kanan lab and ab initio simulations in the Martinez lab to elucidate the chemical principles of carbonate-catalyzed CO<sub>2</sub> hydrogenations.

The key findings from this research are 1) Alkali carbonates promote CO<sub>2</sub> hydrogenation at intermediate temperatures (200–400 °C) provided there is an appreciable water vapor pressure to form an alkali carbonate hydrate in situ. The hydrate is thought to have higher ion mobility, which is essential for CO<sub>3</sub><sup>2-</sup> to act as a super base. The greatest reactivity is seen with Cs<sub>2</sub>CO<sub>3</sub>, which is the most hygroscopic of the alkali carbonates. 2) At >300 °C and 60 bar total pressure, Cs<sub>2</sub>CO<sub>3</sub> very rapidly and reversibly promotes CO<sub>2</sub> hydrogenation to form formate and oxalate. Isotope exchange experiments and simulations indicate that formate is indeed formed by H<sub>2</sub> deprotonation followed by H<sup>-</sup> attack on CO<sub>2</sub>. At longer reaction times, smaller amounts of other multi-carbon products appear including

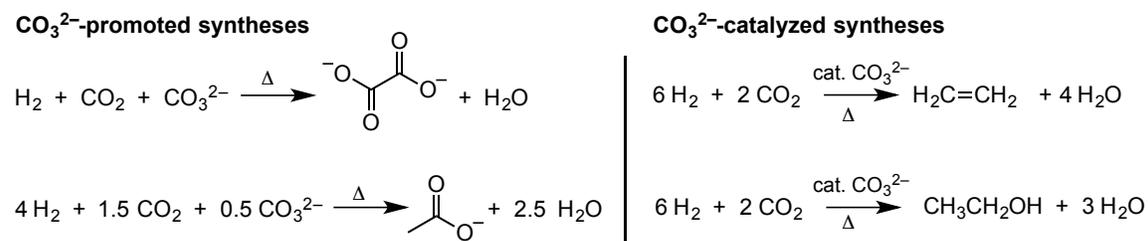
acetate, propionate, succinate and ethylene. Isotope labeling are consistent with acid–base mechanisms for the formation of these higher-order products. 3) Selective CO<sub>2</sub> hydrogenation to oxalate is possible by reacting Cs<sub>2</sub>CO<sub>3</sub> with CO<sub>2</sub> and H<sub>2</sub> followed by CO<sub>2</sub> alone. 4) Concurrent water-gas-shift catalysis by the reactor walls and M<sub>2</sub>CO<sub>3</sub> salts themselves make it difficult to control the H<sub>2</sub>O vapor pressure during batch reactions. Improving the control of this parameter by using a flow reactor is essential for further development of this chemistry.

While the yields of higher-order C<sub>2+</sub> products (acetate, propionate, succinate, ethylene) are currently too low for practical interest, the ability to rapidly and selectively hydrogenate CO<sub>2</sub> to oxalate is of possible interest for ethylene glycol synthesis. This application would require the development of a process to convert cesium oxalate into isolable dimethyl oxalate and regenerate Cs<sub>2</sub>CO<sub>3</sub> using CO<sub>2</sub> and CH<sub>3</sub>OH.

## Introduction

The technologies to extract and process fossil fuels have provided abundant energy and the feedstocks for synthetic chemistry for the past century. While these achievements have transformed society, the enormous rate of fossil fuel consumption that has accompanied these changes is not sustainable because of the accumulation of CO<sub>2</sub> in the atmosphere. Despite the growing awareness of the risk factors of the rising CO<sub>2</sub> levels, high demand for fuels and chemicals will remain for the foreseeable future because modern society has been built on these pillars.<sup>1</sup> One way to address this paradox is to develop an alternative, sustainable production of fuels and chemicals. In principle, it is possible to synthesize these compounds from CO<sub>2</sub>, H<sub>2</sub>O and renewable energy. In practice, such syntheses using existing technologies are far too inefficient and expensive to be viable. If it were possible, however, to “recycle” CO<sub>2</sub> into fuels and chemicals in a way that is competitive with fossil fuel–based production, these processes would be rapidly adopted and scaled because of their dual economic and environmental benefits. We view this prospect as the ultimate synthetic chemistry challenge for sustainability.

This project is pursuing a radically new approach to CO<sub>2</sub> hydrogenation chemistry (CO<sub>2</sub> + H<sub>2</sub> → fuels and chemicals). CO<sub>2</sub> hydrogenation reactions have been known for over a century, but the available methods are only useful for the production of C<sub>1</sub> compounds (e.g. methane, CO, methanol) that are either themselves fossil fuels or very easily produced from these sources.<sup>2-4</sup> As such, CO<sub>2</sub> hydrogenation has not been a competitive method for fuel and chemical production. The ability to hydrogenate CO<sub>2</sub> to produce multi-carbon (C<sub>2+</sub>) compounds could fundamentally change this picture. C<sub>2+</sub> compounds, especially oxygenates, are generally more difficult to produce from fossil fuel sources, more valuable, and have more applications than C<sub>1</sub> compounds. All of the available CO<sub>2</sub> hydrogenation



**Figure 1:** Target CO<sub>2</sub> hydrogenation reactions

catalysts are comprised of transition metals or metal oxides. Selectively hydrogenating CO<sub>2</sub> to a multi-carbon product is enormously challenging because it requires finding a surface that activates CO<sub>2</sub> and H<sub>2</sub> and mediates C–C bond formation in a controlled manner.

Our approach is to use simple acid–base reactions to create a catalytic cycle in which CO<sub>2</sub> is selectively hydrogenated to a high-value C<sub>2+</sub> compound. Prior to the start of the project, we discovered that intermediate temperature (200 °C–350 °C) molten salts containing alkali cations enable CO<sub>3</sub><sup>2-</sup> to deprotonate un-activated C–H bonds, generating carbanion (C<sup>-</sup>) intermediates that undergo C–C bond-forming reactions with CO<sub>2</sub>.<sup>5</sup> The goal of this project was to utilize CO<sub>3</sub><sup>2-</sup> to catalyze CO<sub>2</sub> hydrogenation to produce multi-carbon products. We envisioned that deprotonation of heterolytic activation of H<sub>2</sub> and C–H bonds by CO<sub>3</sub><sup>2-</sup> would provide the reductants and nucleophiles necessary for C–H and C–C bond formation. The specific targets included CO<sub>3</sub><sup>2-</sup>-promoted CO<sub>2</sub> hydrogenations to oxalate and acetate (these reactions consume CO<sub>3</sub><sup>2-</sup>) and CO<sub>3</sub><sup>2-</sup>-catalyzed CO<sub>2</sub> hydrogenations to ethylene and ethanol (**Figure 1**). Our research combined experimental studies in the Kanan lab with *ab initio* molecular dynamics simulations in the Martinez lab.

## Background

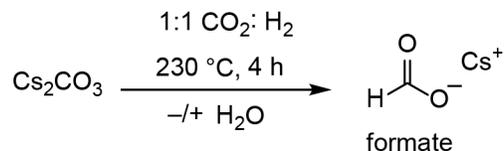
There is growing interest in the development of CO<sub>2</sub> hydrogenation catalysts that selectively produce multi-carbon products. Researchers have recently reported Fe- and Co-based catalysts that produce substantial fractions of higher-order alkanes (C<sub>5+</sub>)<sup>6–8</sup> or light olefins (ethylene, propylene)<sup>9</sup>. While these advances are promising, further improvement is needed to address the problems of competitive CH<sub>4</sub> production and deactivation by H<sub>2</sub>O. For multi-carbon oxygenates, recent reports have described both heterogeneous and homogeneous precious metal catalysts that hydrogenate CO<sub>2</sub> to ethanol with high selectivity at moderate CO<sub>2</sub> conversion.<sup>10–12</sup> These experiments were performed in batch reactors using a solvent (organic or water). If these catalysts can be utilized in flow reactors without a solvent, they would be a starting point for the development of a scalable process. Accessing carboxylic acids has been more difficult, however, with only one study reporting low levels of acetic acid production.<sup>13</sup>

## Results

### *Experimental Studies of Carbonate-Promoted CO<sub>2</sub> Hydrogenation*

Our experimental results are described in detail in our recent publication.<sup>14</sup> Here we briefly summarize the key findings.

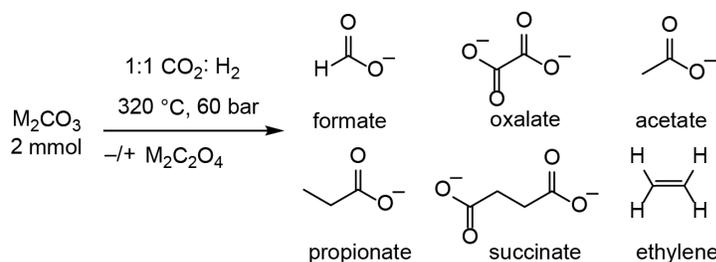
Solid alkali carbonates are ordinarily inert crystalline solids at temperatures below their melting points (which are >800 °C). We hypothesized that the presence of water vapor at intermediate temperatures (200–400 °C) would lead to the formation of alkali carbonate hydrates (M<sub>2</sub>CO<sub>3</sub>•*n*H<sub>2</sub>O) that would exhibit increased ion mobility, thereby enabling CO<sub>3</sub><sup>2-</sup> to heterolytically activate H–H and C–H bonds. We first investigated CO<sub>2</sub> hydrogenation reactions in which Cs<sub>2</sub>CO<sub>3</sub> was subjected to CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O at 230 °C and ~30 bar total pressure. The key results are summarized in **Figure 2**. At this temperature, formate (HCO<sub>2</sub><sup>-</sup>) and CO were the only observed products. CO was produced by background reverse-water-gas-shift catalysis from the stainless steel reactor walls and by the M<sub>2</sub>CO<sub>3</sub> salt. The addition of several bar of H<sub>2</sub>O pressure had a dramatic effect on the yield of formate, which was produced solely by the Cs<sub>2</sub>CO<sub>3</sub>.



Entry	Cs <sub>2</sub> CO <sub>3</sub>	p <sub>H<sub>2</sub>O</sub>	p <sub>total</sub>	formate	CO
1	10 mmol	—	25 bar	79 μmol	830 μmol
2	10 mmol	6 bar	31 bar	605 μmol	120 μmol
3	—	—	25 bar	—	290 μmol
4	—	6 bar	33 bar	—	50 μmol

**Figure 2:** Cs<sub>2</sub>CO<sub>3</sub>-promoted CO<sub>2</sub> hydrogenation with and without added H<sub>2</sub>O. Ref. 14

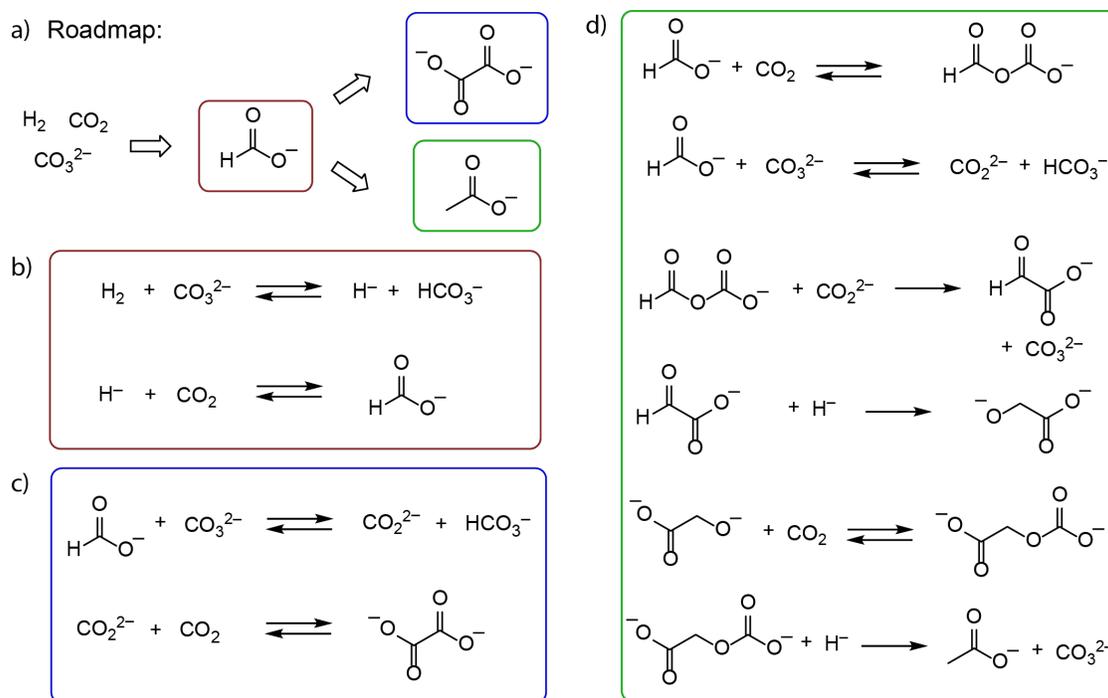
At higher temperatures and pressures, a substantial pressure of H<sub>2</sub>O was produced by reverse-water-gas-shift catalysis by the reactor walls and M<sub>2</sub>CO<sub>3</sub> salt, obviating the need to add H<sub>2</sub>O to access a reactive carbonate species. Under these conditions, much higher yields of carboxylates (with respect to M<sub>2</sub>CO<sub>3</sub>) were observed. The major product remained formate, but substantial quantities of oxalate and smaller amounts of other multi-carbon products were also observed (**Figure 3**). Seeding the M<sub>2</sub>CO<sub>3</sub> salt with oxalate to begin with improved the yields of the other carboxylates.



Entry	M <sup>+</sup>	(M <sup>+</sup> ) <sub>2</sub> oxalate	t	formate	oxalate	acetate	propionate	succinate	ethylene
1	Cs <sup>+</sup>	—	5 min	1.4 mmol	413 μmol	9 μmol	1 μmol	1 μmol	21 μmol
2	Cs <sup>+</sup>	—	2 h	1.8 mmol	300 μmol	23 μmol	7 μmol	9 μmol	21 μmol
3	Cs <sup>+</sup>	—	8 h	1.9 mmol	371 μmol	50 μmol	34 μmol	31 μmol	22 μmol
4	Cs <sup>+</sup>	75 μmol	8 h	2.2 mmol	278 μmol	274 μmol	125 μmol	85 μmol	247 μmol
5	Cs <sup>+</sup>	500 μmol	8 h	2.4 mmol	438 μmol	42 μmol	38 μmol	31 μmol	111 μmol
6	Rb <sup>+</sup>	—	8 h	447 μmol	120 μmol	39 μmol	7 μmol	14 μmol	40 μmol
7	K <sup>+</sup>	—	8 h	28 μmol	—	34 μmol	4 μmol	—	116 μmol

**Figure 3:** CO<sub>3</sub><sup>2-</sup>-promoted CO<sub>2</sub> hydrogenation at ≥ 300 °C. Ref. 14.

We performed a series of isotope exchange experiments to investigate the mechanistic pathways for  $\text{CO}_3^{2-}$ -promoted  $\text{CO}_2$  hydrogenation to multi-carbon carboxylates. A mechanistic scheme for the formation of formate, oxalate, and acetate that is consistent with our isotope data is shown in **Figure 4**. Proposed mechanisms for the additional products are described in the paper.<sup>14</sup> In essence, we propose that hydrated alkali carbonates are super-bases at intermediate temperatures, deprotonating H–H and C–H bonds to generate hydride ( $\text{H}^-$ ) and carbanion nucleophiles that participate in the key C–H and C–C bond-forming events.



**Figure 4: Proposed pathways.** a) roadmap and proposed mechanistic pathway for formation of b) formate c) oxalate and d) acetate via  $\text{CO}_3^{2-}$ -promoted  $\text{CO}_2$  hydrogenation. Ref. 14

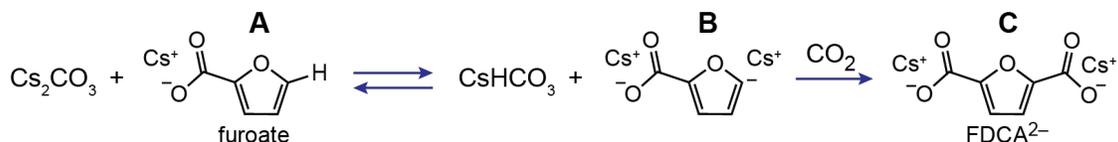
Selective production of oxalate from  $\text{CO}_2$  hydrogenation is an appealing target because dimethyl oxalate can be selectively hydrogenated to ethylene glycol or to ethanol using Cu catalysts.<sup>15,16</sup> We therefore investigated conditions to optimize oxalate production and suppress the other carboxylate products. A two-step sequence in which  $\text{Cs}_2\text{CO}_3$  was reacted with a 1:1 mixture of  $\text{CO}_2:\text{H}_2$  at 60 bar and 340 °C followed by only  $\text{CO}_2$  at the same temperature and pressure resulted in 42% yield of oxalate (with respect to  $\text{CO}_3^{2-}$ ) and essentially no other carboxylate products.

The formation of carboxylate products results in the consumption of  $\text{CO}_3^{2-}$ . Ideally it would be possible to generate a neutral isolable product and render the chemistry catalytic in  $\text{CO}_3^{2-}$ . Ethylene was observed as a very minor product in the  $\text{CO}_2$  hydrogenation reactions, suggesting that a closed cycle is possible. In addition, we obtained evidence that carboxylates are in equilibrium with volatile carboxylic acids under the  $\text{CO}_2$  hydrogenation conditions by using isotopically labeled acetate as a tracer. These results raise the

possibility of performing carbonate-catalyzed CO<sub>2</sub> hydrogenation in a flow reactor and sweeping away volatile carboxylic acids to enable catalytic turnover.

### *Simulations in the Nanoreactor*

To gain insight into carbonate-promoted C–H carboxylation, we used nanoreactor simulations to construct a reaction network for furoate carboxylation because there is a large amount of experimental data for evaluation of the computational results. Discovered reactions were refined to obtain minimal energy paths, barrier heights, and reaction rate constants (using transition state theory). With this information, we performed kinetics simulations to address the time evolution of intermediates and products in the reaction mixture. These simulations found that the main mechanism for carboxylation is deprotonation followed by attack of the carbanion on CO<sub>2</sub>, consistent with the mechanism proposed based on the experimental data (**Figure 5**). The simulations also found that the selectivity for furan-2,5-dicarboxylic acid vs 2,3- or 2,-4 isomers is very high.



**Figure 5:** Major pathway for C–H carboxylation of furoate (A) uncovered by *nanoreactor* simulations.

We also investigated the effect of CO<sub>2</sub> pressure on the reaction. The following equilibrium is expected in molten carbonate salts:



Although this reaction is favorable, carbonate anions will not be depleted by this reaction if the solvated CO<sub>2</sub> concentration is very low. Although the nanoreactor did find a pathway for deprotonation of furoate by C<sub>2</sub>O<sub>5</sub><sup>2-</sup>, the barrier is quite high and this reaction was insignificant in the kinetics simulations. Instead, CO<sub>3</sub><sup>2-</sup> was found to be the primary base. This result predicts that increasing CO<sub>2</sub> pressure will slow down deprotonation (since it will lead to C<sub>2</sub>O<sub>5</sub><sup>2-</sup>). However, the net effect may be rather complicated since the subsequent carboxylation step requires CO<sub>2</sub>.

CO<sub>2</sub> hydrogenation was evaluated by combining Cs<sub>2</sub>CO<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub> in the nanoreactor. The simulations found that H<sub>2</sub> deprotonation by CO<sub>3</sub><sup>2-</sup> is fast and reversible and that H<sup>-</sup> attack on CO<sub>2</sub> to form formate is also fast and reversible, consistent with the proposal in **Figure 4b**. Interestingly, the nanoreactor did not find a pathway to oxalate involving CO<sub>2</sub>, contradicting the proposal in **Figure 4c**. The only pathway to oxalate found in the simulations involved a direct attack of CO on CO<sub>3</sub><sup>2-</sup>. Researchers have previously reported the synthesis of oxalate from Cs<sub>2</sub>CO<sub>3</sub> under a mixture of CO and CO<sub>2</sub> at 380 °C and 200 bar (in the absence of H<sub>2</sub>).<sup>17</sup> However, oxalate formation via CO attack on CO<sub>3</sub><sup>2-</sup> is difficult to reconcile with our experimental CO<sub>2</sub> hydrogenation conditions and our isotope exchange experiments.<sup>14</sup>

### **Conclusions**

Our studies have found that hydrated alkali carbonate salts promote a very rapid hydrogenation of CO<sub>2</sub> to formate and oxalate at intermediate temperature and pressure.

These transformations are enabled by the remarkable ability of mobile  $\text{CO}_3^{2-}$  ions to deprotonate H–H and C–H bonds in alkali-rich media at intermediate temperatures. Translation to a scalable process faces a number of challenges, foremost of which is closing the cycle to produce a neutral product and regenerate  $\text{CO}_3^{2-}$ . Given the demonstrated ability to produce oxalate selectively, a potentially fruitful direction is to investigate ways to convert cesium oxalate into dimethyl oxalate and regenerate  $\text{Cs}_2\text{CO}_3$  using only  $\text{CO}_2$  and  $\text{CH}_3\text{OH}$ . If this transformation could be performed efficiently, the carbonate-promoted hydrogenation described here could be in principle be combined with Cu-catalyzed dimethyl oxalate hydrogenation to effect a selective synthesis of ethylene glycol or ethanol from  $\text{CO}_2$  and  $\text{H}_2$ .

## Publications and Presentations

### Publications

1. Dick, G. R.; Frankhouser, A. D.; Banerjee, A.; Kanan, M. W. [A Scalable Carboxylation Route to Furan-2,5-Dicarboxylic Acid](#). *Green Chemistry* **19**:13, 2966-2972 (2017). DOI: 10.1039/C7GC01059A
2. Banerjee, A.; Kanan, M. W. [Carbonate-Promoted Hydrogenation of Carbon Dioxide to Multi-Carbon Carboxylates](#). *ACS Central Science* **4**:5, 606-613 (2018). DOI: 10.1021/acscentsci.8b00108
3. Xiao, D. J.; Chant, E. D.; Frankhouser, A. D.; Chen, Y.; Yau, A.; Washton, N.; Kanan, M. W. Carbonate-Catalyzed Esterification of Aromatic Hydrocarbons with  $\text{CO}_2$  and Alcohol. *Submitted* (2019).

### Presentations

1. Banerjee, A. Carbon Dioxide Utilization via Carbonate-Promoted C–H Carboxylation. Oral Presentation at the ACS National Meeting, San Diego, March 2016.
2. Kanan, M. W. Sustainable Carbon–Carbon Bond Formation. Invited Talk at Nature Conference on Materials for Energy. Wuhan, China, June 2016.
3. Kanan, M. W. Carbonate-Catalyzed  $\text{CO}_2$  Utilization. Invited Talk at the SERC Conference, Chapel Hill NC, October 2016.
4. Kanan, M. W. Carbonate-Catalyzed  $\text{CO}_2$  Utilization. Invited Talk at Korea Advanced Institute of Science and Technology. Daejeon, South Korea, February 2017.
5. Kanan, M. W. Carbonate-Catalyzed  $\text{CO}_2$  Utilization. Invited Plenary Talk at International Solar Fuels Conference Young Meeting, San Diego, July 2017.

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Provide the references for your work using endnote, not footnote, notation.

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