Final Technical Report

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Project Title: Carbonate-Catalyzed CO_2 Insertion into Hydrocarbon C-H Bonds
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Abstract: The development of methods to utilize CO_2 as a feedstock for chemical and fuel synthesis is critical for creating renewable alternatives to fossil fuel-based products. This project investigated a class of catalyst materials known as "dispersed carbonates", which are composed of alkali carbonate salts (e.g. potassium carbonate) dispersed in porous support materials. These catalysts react with CO_2 and organic molecules to form chemicals known as carboxylates that have wide applications in the chemical industry. The project used a combination of spectroscopic and reactivity studies to provide fundamental insight into the structure and mechanism of dispersed carbonates in these reactions, leading to variants with greater reactivity. In addition, dispersed carbonates were investigated for CO_2 hydrogenation catalysis, which is critical for processes under development for making sustainable fuels. The dispersed carbonates proved to be highly active and selective catalysts for the reverse water gas shift reaction in which CO_2 is hydrogenated to CO. The dispersed carbonates provide a compelling alternative to conventional metal-based catalysts for reverse water gas shift that could enable new process designs with higher efficiency and lower complexity.

Objectives: The major goals of this project were to i) obtain fundamental insight into the structure and dynamics of solid base materials comprised of alkali carbonates dispersed in mesoporous supports; ii) probe mechanisms of CO_3^{2-}-promoted C–H carboxylation and CO_2-promoted methylation reactions with these materials; iii) design and synthesize more active variants.

Background: As brief background, the catalytic materials consist of an alkali carbonate dispersed into a mesoporous support. Nanoconfinement in the mesopores of the support material disrupts the crystallinity of the alkali carbonate, resulting in an amorphous material that exhibits super-basic reactivity at elevated temperature. The first study of the synthesis, characterization, and hydrocarbon C–H carboxylation/methylation chemistry catalyzed by these materials was published just prior to the start of this project (Xiao, Chant, Frankhouser, Chen, Yau, Washton, Kanan Nat. Chem. **2019**, *10*, 940-947). This study focused on Cs_2CO_3 and K_2CO_3 dispersed in mesoporous TiO_2 (Cs_2CO_3/TiO_2 and K_2CO_3/TiO_2, respectively). Structural characterization using a combination of synchrotron powder x-ray diffraction, variable temperature solid-state NMR, and ambient temperature IR established the amorphous nature of the dispersed carbonates. In the ambient temperature IR, the region corresponding to the C–O stretching vibration showed a peak splitting indicative of bidentate or unidentate CO_3^{2-} binding to the alkali cation. When exposed to benzene and CO_2 at elevated temperature and pressure (400 °C, 30 bar), the dispersed carbonates promote benzene C–H carboxylation to form benzoate and smaller amounts of di- and tri-carboxylates. The carboxylate products are dispersed in the mesoporous support along with remaining unreacted carbonate. When this product mixture is exposed to flowing CH_3OH-saturated CO_2 at 280 °C, the benzoate is converted into methyl benzoate, which is volatilized and isolated with a cold trap. This methylation reaction regenerates the dispersed carbonate, which can be reused for at least 10 cycles of carboxylation/methylation without any performance degradation.

Publications: Research supported by this award led to 3 peer-reviewed journal articles and 1 patent application:
<u>Journal Articles</u>
1. Carbonate-promoted C–H Carboxylation of Electron-Rich Heteroarenes. Porter & Kanan, Chem. Sci. **2020**, *11*, 11936-11944.

2. Carbonate-Catalyzed Reverse Water-Gas Shift to Produce Gas Fermentation Feedstocks for Renewable Liquid Fuel Synthesis. Li, Frankhouser & Kanan, Cell Rep. Phys. Sci. **2022**, *3*, 101201.
3. Improving Carbonate-Promoted C–H Carboxylation Using Mesoporous Carbon Supports. Chant, Li & Kanan, ACS Sust. Chem. Eng. **2023**, *11*, 5876-5882.
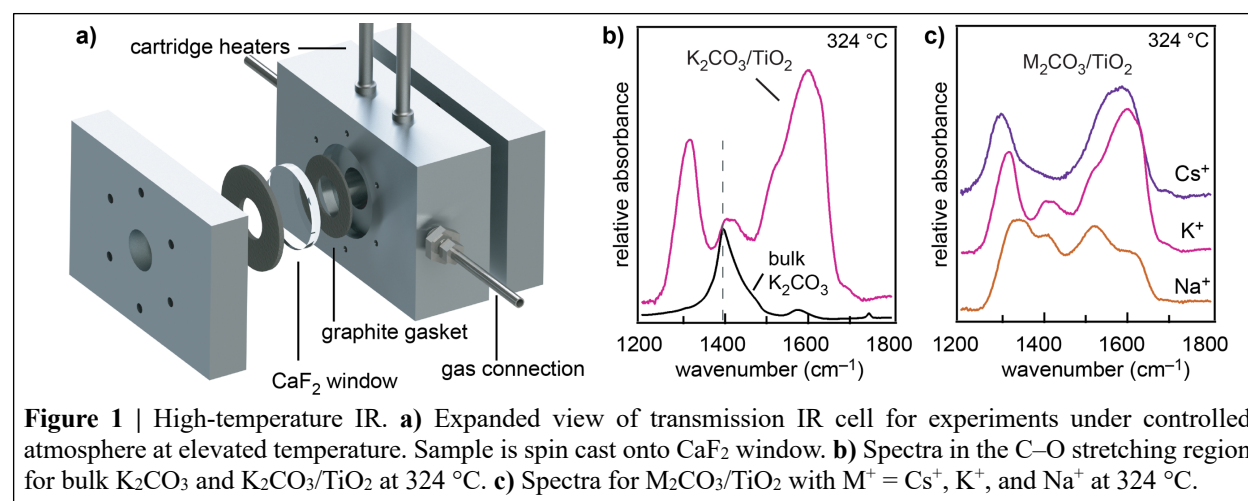Patent Application
1. Dispersed Carbonate Catalysts for the Reverse Water Gas Shift Reaction. Kanan, Li & Frankhouser, International Patent Application PCT/US22/25361, April 19, 2022.

Accomplishments: The project achieved substantial progress toward the main objectives listed above. In addition to C–H carboxylation, which was the focus, the project advanced the use of dispersed carbonate materials as catalysts for the reverse water-gas-shift reaction. The major accomplishments are summarized below, with full details provided in the publications.
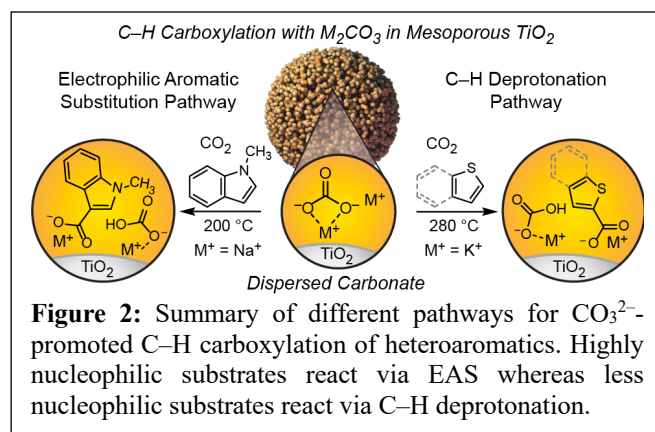
Structure and dynamics of dispersed carbonates

To probe the local structure of dispersed carbonates at C–H carboxylation-relevant temperatures, we designed and built a custom transmission IR cell (**Figure 1a**). The gas-tight cell is equipped with two cartridge heaters and contains inlet and outlet ports to enable the atmosphere to be changed during an experiment. Samples are spin-cast onto a CaF_2 window held between graphite gaskets. The heaters can take the cell up to 400 °C, which corresponds to a window (sample) temperature of 324 °C. **Figure 1b** shows the C–O stretching (ν_3) region of the spectrum for K_2CO_3/TiO_2 at 324 °C overlaid on the spectrum for bulk K_2CO_3 powder for reference. Whereas bulk K_2CO_3 has one major band with a peak at 1395 cm^{-1}, the spectrum for K_2CO_3/TiO_2 shows two major bands with peaks at 1300 cm^{-1} and 1600 cm^{-1} and a smaller band at 1400 cm^{-1}. The smaller band at 1400 cm^{-1} likely includes a contribution from a minor amount of bulk K_2CO_3 domains (nanocrystallites). Structural interpretation of the other bands is guided by previous IR studies of CO_3^{2-}-containing coordination complexes with well-defined structures determined by XRD and previous studies of CO_2 adsorbed onto reactive oxide surfaces (Busca & Lorenzelli, Mater. Chem. **1982**, 7, 89-126; Nakamoto, Fujita, Tanaka & Kobayashi, J. Am. Chem. Soc. **1957**, *79*, 4904-4908). The prominent bands at 1300 cm^{-1} and 1600 cm^{-1} are consistent with CO_3^{2-} bound either in a bidentate fashion to a weakly polarizing cation such as an alkali cation or in a unidentate fashion to a more polarizing cation such as Ti^{4+}. The band at 1600 cm^{-1} contains multiple overlapping features, suggesting that additional coordination modes are present. Overall, the 324 °C spectrum confirms that the K_2CO_3 in K_2CO_3/TiO_2 retains a predominantly amorphous structure at temperatures relevant to C–H carboxylation.

Figure 1 | High-temperature IR. a) Expanded view of transmission IR cell for experiments under controlled atmosphere at elevated temperature. Sample is spin cast onto CaF_2 window. **b)** Spectra in the C–O stretching region for bulk K_2CO_3 and K_2CO_3/TiO_2 at 324 °C. **c)** Spectra for M_2CO_3/TiO_2 with $M^+ = Cs^+$, K^+, and Na^+ at 324 °C.

Figure 1c shows a comparison of the IR spectra in C–O stretching region for Na_2CO_3/TiO_2, K_2CO_3/TiO_2, and Cs_2CO_3/TiO_2 at 324 °C. As seen for K_2CO_3/TiO_2, the spectrum for Cs_2CO_3/TiO_2 has two major bands with peaks at 1300 cm^{-1} and 1600 cm^{-1}. These features are considerably broader for Cs_2CO_3/TiO_2, which may reflect a greater diversity of CO_3^{2-} coordination environments. Notably, there is no peak in the 1400 cm^{-1} region, indicating the absence of bulk domains. K_2CO_3/TiO_2 and Cs_2CO_3/TiO_2 show comparable reactivity for C–H carboxylation of benzene and benzothiophene. Mechanistic experiments for both substrates support a carboxylation pathway that proceeds through initial C–H deprotonation (Nat. Chem. **2019**, *10,* 940-947; Chem. Sci. **2020**, *11*, 11936-11944). We hypothesize that the species corresponding to the major peaks at 1300 cm^{-1} and 1600 cm^{-1} (i.e. the putative bidentate coordinated CO_3^{2-}) is a reactive solid base for C–H deprotonation. In support of this hypothesis, the spectrum for Na_2CO_3/TiO_2 is qualitatively different from K_2CO_3/TiO_2 and Cs_2CO_3/TiO_2. There are four overlapping bands with two major peaks at 1325 cm^{-1} and 1510 cm^{-1} and somewhat smaller peaks at 1400 cm^{-1}, and 1620 cm^{-1}. The large spectral differences are reflected in reactivity – Na_2CO_3/TiO_2 shows very low reactivity for C–H carboxylation of benzene and benzothiophene. Interestingly, however, Na_2CO_3/TiO_2 is much more reactive toward carboxylation of 1-methylindole, which reacts instead through and electrophilic aromatic substitution pathway.

Mechanisms and expansion of substrate scope for C–H carboxylation

To gain insight into the mechanism(s) of C–H carboxylation, we examined the dependence on C–H acidity by performing a study with a collection of aromatic heterocycles including thiophene, benzothiophene, phenyl thiophene, and 1-methylindole. We calculated the gas-phase heterolytic bond dissociation enthalpies (gas phase acidities) of the C–H bonds in these substrates and compared them to the C–H bond in benzene. The most acidic C–H bonds in each heterocycle was found to be more acidic than benzene by 15–20 kcal/mol, while the separation between the two most acidic bonds in each substrate was 5–8 kcal/mol. While more acidic than benzene, all of these substrates require the use of very strong bases (e.g. BuLi) to deprotonate them in solution. We then assessed their reactivity in carbonate-promoted C–H carboxylation using Cs_2CO_3/TiO_2 and K_2CO_3/TiO_2. All substrates underwent C–H carboxylation in substantially higher yield than benzene at 100–200 °C lower temperature. For the sulfur heterocycles, the major product was the carboxylate resulting from C–H carboxylation at the most acidic C–H bond. By optimizing the conditions, highly selective carboxylation was possible with both benzothiophene and phenyl thiophene. Thiophene itself was prone to decomposition pathways that resulted in a less selective carboxylation reaction.

Figure 2: Summary of different pathways for CO_3^{2-}-promoted C–H carboxylation of heteroaromatics. Highly nucleophilic substrates react via EAS whereas less nucleophilic substrates react via C–H deprotonation.

Interestingly, methylindole underwent preferential C–H carboxylation at the less acidic C3 C–H bond. Furthermore, KIE measurements using competition experiments revealed a relatively large primary KIE for benzothiophene C–H carboxylation and essentially no KIE for methylindole carboxylation. We concluded that the methylindole reacts via an electrophilic aromatic substitution (EAS) pathway wherein pi attack on CO_2 precedes C–H deprotonation. This pathway is evidently assisted by the dispersed carbonate as no reaction was observed with M_2CO_3 powders. DFT

calculations indicated a barrier of ~30 kcal/mol for the initial pi attack and a very unstable zwitterionic intermediate. The EAS pathway is favored over the C–H deprotonation pathway for 1-methylindole because this substrate is a substantially more reactive pi nucleophile. In addition to the C–H carboxylation studies, we also developed a new protocol for methylation and M_2CO_3/TiO_2 regeneration using neat dimethyl carbonate. As a demonstration, we performed 5 cycles of C–H carboxylation/methylation to transform benzothiophene into methylbenzothiophene-2-carboxylate. Full details of this work are described in Chem. Sci. **2020**, *11*, 11936-11944.

Improving C–H carboxylation activity

The initial development of dispersed carbonates for C–H carboxylation focused on materials prepared with oxide supports. While robust, these materials exhibited relatively low *carbonate conversion* – the % of the dispersed carbonate that was consumed to form carboxylate products. To probe the effects of the support material, we performed a study comparing mesoporous oxides with mesoporous carbon materials for C–H carboxylation reactions with benzene and benzothiophene substrates. Using established templating procedures, mesoporous carbons were prepared with a range of pore size distributions. Cs_2CO_3 was dispersed into the mesoporous carbons using methanolic solutions and the resulting materials were compared to Cs_2CO_3 loaded into mesoporous TiO_2, ZrO_2, and Al_2O_3. For both benzene and benzothiophene, 2-4× higher carbonate conversions were observed for the mesoporous carbons than any of the oxide supports. This result was obtained across different pore structures (ordered vs disordered) and pore size distributions, indicating that the carbonates dispersed on carbon surfaces are intrinsically more reactive than on oxide surfaces. We postulate that the carbonate-support surface interaction is weaker with carbon supports, leading to greater carbonate mobility that enables higher carbonate conversion. Unfortunately, carboxylate products cannot be methylated using CO_2/methanol with carbon supports, possibly because the carbon support does not catalyze the formation of the putative (di)methyl carbonate reactive methylating species. Use of neat dimethyl carbonate, however, proved to be effective for converting carboxylate products into isolable methyl esters and regenerating dispersed carbonates in mesoporous carbons. Full details are available in ACS Sust. Chem. Eng. **2023**, *11*, 5876-5882.

Carbonate-Catalyzed Reverse Water-Gas Shift

In parallel with C–H carboxylation studies, dispersed carbonates were investigated for CO_2 hydrogenation catalysis. Interestingly, benzene and H_2 have the same gas phase acidity. We therefore reasoned that dispersed carbonates would be able to heterolytically activate H_2 in the presence of CO_2 under similar conditions in which they promote benzene C–H carboxylation. CO_2 hydrogenation studies were performed using a custom fixed bed reactor, focusing on temperatures ranging from 350 °C to 500 °C and 10 bar pressure. The dispersed carbonate catalysts proved to be highly active for the reverse water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) beginning at 425 °C and essentially 100

Figure 3: Schematic of proposed mechanism for RWGS catalyzed by dispersed carbonates
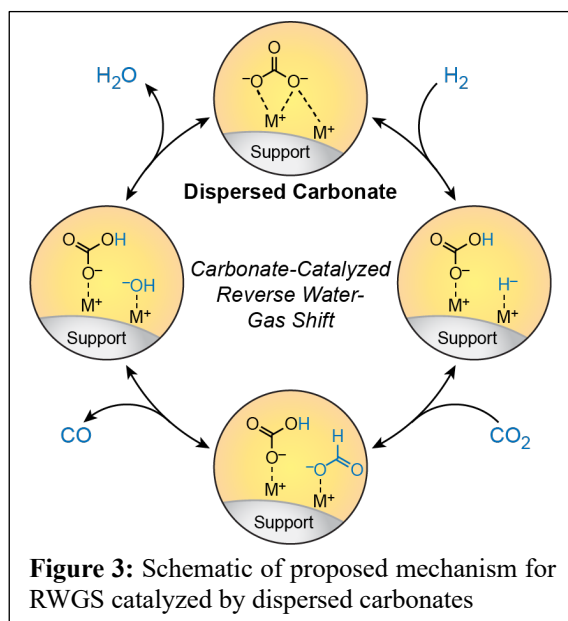
% selective for this reaction. This high selectivity is remarkable because the methanation reaction is strongly thermodynamically favored over RWGS in this temperature regime. We postulate that dispersed carbonates catalyze RWGS via deprotonation of H_2 to form hydride (H^-), reaction of H^- with CO_2 to form formate (HCO_2^-), and rearrangement of formate to form CO and OH^-, which combines with the proton to form H_2O (**Figure 3**). The catalysts resist methanation because there is no transition metal to bind CO to enable further reduction. Full details of our initial study of RWGS with dispersed carbonates are available in Cell Rep. Phys. Sci. **2022**, *3*, 101201.

Dispersed carbonate RWGS catalysts are of substantial interest for application in sustainable fuel production systems combining RWGS with Fischer-Tropsch (FT) catalysis. Current RWGS technologies utilize Ni catalysts that are commonly used in steam reforming. These materials catalyze not just RWGS but also methane (CH_4) and coke (graphitic carbon) formation. To suppress methane and avoid coking, conventional Ni RWGS catalysts must be operated at very high temperatures (typically >900 °C) where RWGS is thermodynamically favored over these competing reactions. This temperature regime necessitates expensive materials of construction and complicates heat integration with FT. Dispersed carbonates provide a highly selective RWGS at intermediate temperatures, which enables simpler reactor materials and could enable new RWGS/FT process designs with improved efficiency.