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Cascade Catalysis for the Homogeneous Hydrogenation of CO_2 to Methanol

Chelsea A. Huff and Melanie S. Sanford*

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, United States

Supporting Information

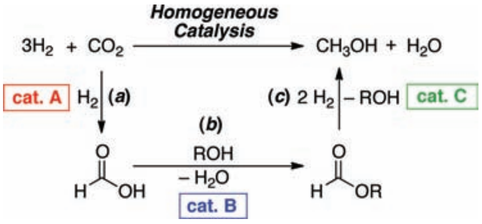
ABSTRACT: This communication demonstrates the homogeneous hydrogenation of CO_2 to CH_3OH via cascade catalysis. Three different homogeneous catalysts, $(PMe_3)_4Ru(Cl)(OAc)$, $Sc(OTf)_3$, and (PNN)Ru(CO)(H), operate in sequence to promote this transformation.

The global demand for energy is increasing rapidly as a result of population and economic growth. Currently, the vast majority of energy usage involves the combustion of nonrenewable fossil fuels, which is leading to unsustainable increases in anthropogenic emissions of CO_2.[1] As a result, the identification of carbon-neutral alternatives to fossil feedstocks is a critical goal for the scientific community.[2] One attractive approach would involve the hydrogenation of CO_2 (captured from the atmosphere)[3] with H_2 (ideally derived from a renewable source)[4] to produce methanol.[5] This overall process would be carbon-neutral, and the product is both a potential gasoline replacement[5] and a starting material for the synthesis of important platform chemicals, including ethylene and propylene.[6]

Previous work in this area has focused on developing single catalysts that promote the multistep sequence of reduction reactions required to transform CO_2 into CH_3OH. For example, Cu-based heterogeneous catalysts for the reaction of CO_2 with H_2 to form CH_3OH and H_2O have been reported.[7,8] However, these systems suffer from the significant disadvantage that they require high operating temperatures (200−250 °C), which limits the theoretical yield of the entropically disfavored reduction products.[9] In addition, rational tuning of the reactivity and selectivity of heterogeneous catalysts remains challenging.[9] For these reasons, significant recent work has aimed at the development of homogeneous catalysts for the low(er) temperature conversion of CO_2 to methanol.[10−13] Several such systems that operate at room temperature and contain tunable supporting ligands have been reported.[11a,12b] However, current catalysts generally remian limited by the requirement for impractical and expensive hydrogen sources such as boranes and hydrosilanes.[8,11,12]

We sought to address these challenges by exploiting cascade catalysis[14,15] for the homogeneous catalytic reduction of CO_2 with H_2 to produce CH_3OH. This approach involves the use of a series of different homogeneous catalysts operating in a single vessel to promote the various steps of the CO_2 reduction sequence. Importantly, our strategy precludes the requirement of isolating thermodynamically disfavored and/or chemically unstable intermediates (e.g., HCO_2H or HCOH, respectively). Furthermore, it offers the distinct advantage that the rate and selectivity of each step can potentially be tuned by simply substituting an alternative catalyst. The major challenge for this approach is to identify a series of catalysts that are compatible with one another, operate effectively under the same reaction conditions, and are not poisoned by catalytic intermediates and/or products. This communication demonstrates the viability of this approach for the hydrogenation of CO_2 to CH_3OH using $(PMe_3)_4Ru(Cl)(OAc)$, $Sc(OTf)_3$, ROH, and (PNN)Ru(CO)(H) as catalysts.

Scheme 1. Proposed Sequence for Converting $CO_2 + H_2$ to $CH_3OH + H_2O$



We first targeted a cascade catalysis sequence involving: (*a*) hydrogenation of CO_2 to formic acid, (*b*) esterification to generate a formate ester, and (*c*) hydrogenation of the ester to release methanol (Scheme 1). Steps (*a*) and (*b*) have been demonstrated previously with several different homogeneous catalysts (albeit at high CO_2 pressures).[16−19] In contrast, when we began this work, homogeneous hydrogenation of formate esters (step *c*) had little precedent in the literature.[20] Thus, we first sought to establish whether Ru complexes **C-1**−**C-3** (which are known to catalyze the hydrogenation of alkyl esters and amides to alcohols)[21−23] could promote the reaction of H_2 with methyl formate to afford 2 equiv of CH_3OH. Gratifyingly, **C-1** and **C-2** both showed high activity for this transformation at 135 °C under 5 bar H_2 (Table 1, entries 1 and 2). Notably, similar results were disclosed in a very recent publication by Milstein.[24]

A key requirement for the cascade catalysis sequence in Scheme 1 is that the formate ester hydrogenation catalyst be compatible with CO_2. Initial studies suggested that this might be problematic. For example, the **C-1**-catalyzed hydrogenation of methyl formate in the presence of 5 bar H_2/30 bar CO_2 produced only a 17% yield of methanol, versus a yield of 98% under otherwise analogous conditions but without CO_2 (Table 1, entries 4 and 1, respectively). Furthermore, treatment of **C-2** with 1 atm CO_2 at 25 °C resulted in the appearance of at least nine new Ru hydride species (as determined by ^1H NMR spectroscopic

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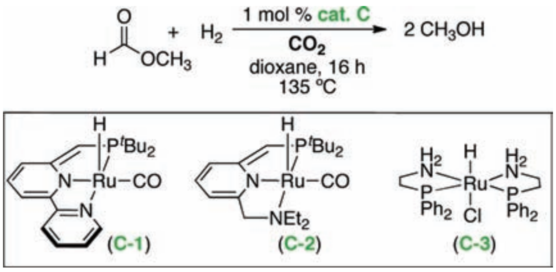
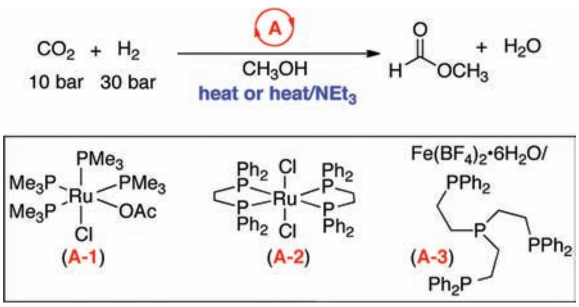
Table 1. Hydrogenation of HCO_2CH_3 in the Presence of CO_2[a]



entry	catalyst	$P_{H_2}:P_{CO_2}$[b]	conv. of HCO_2CH_3	yield of CH_3OH
1	**C-1**	5:0	98%	98%
2	**C-2**	5:0	99%	102%
3[c]	**C-3**	5:0	100%	<3%[d]
4	**C-1**	5:35	54%	17%
5	**C-1**	20:20	85%	76%
6	**C-1**	30:10	97%	97%
7	**C-2**	30:10	43%	16%

[a] Conditions: 0.01 mmol of catalyst **C**, 1 mmol of methyl formate, 1 mL of dioxane. [b] Pressures in bar. [c] 1 mmol of KOtBu was added under otherwise identical conditions. [d] The major organic product was methyl *tert*-butyl ether.

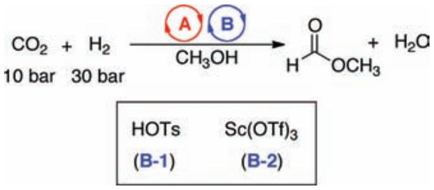
Table 2. Conversion of CO_2 to HCO_2CH_3: Thermal Esterification with and without NEt_3[a]



entry	catalyst **A**/additive	TON
1	**A-1**/none	3
2	**A-2**/none	1
3	**A-3**/none	10
4[b]	**A-1**/NEt_3	18
5[b]	**A-2**/NEt_3	21
6[b]	**A-3**/NEt_3	21

[a] Conditions: 0.0126 mmol of catalyst **A**, 2 mL of CH_3OH, 16 h, 135 °C. [b] 0.2 mL of NEt_3 was added under otherwise identical conditions.

Table 3. Conversion of CO_2 to HCO_2CH_3: Lewis/Brønsted Acid Catalysts[a]



entry	catalyst **A**/**B**	TON
1	**A-1**/**B-1**	11
2	**A-2**/**B-1**	10
3	**A-3**/**B-1**	13
4	**A-1**/**B-2**	40
5	**A-2**/**B-2**	16
6	**A-3**/**B-2**	5

[a] Conditions: 0.0126 mmol of catalysts **A** and **B**, 2 mL of CH_3OH, 16 h, 135 °C.

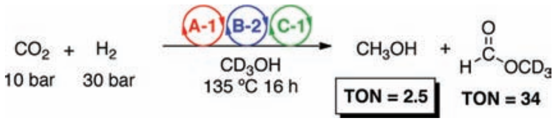
analysis of the crude mixture; see Figure S6 in the Supporting Information), indicating the potential for CO_2 to divert the proposed catalytically active species. We reasoned that increasing the partial pressure of H_2 in the gas mixture would enhance the rate of the desired hydrogenation process relative to catalyst inhibition/deactivation pathways. Gratifyingly, moving to a 30 bar H_2/10 bar CO_2 mixture resulted in a 97% yield of CH_3OH (entry 6).

With the conditions for step *c* in hand, we next focused on steps *a* and *b* of the proposed cascade reduction sequence. A number of catalysts (e.g., **A-1**, **A-2**, and **A-3** in Table 2)[17−19] are known to convert CO_2, H_2, and CH_3OH to HCO_2CH_3. However, these reactions typically require high CO_2 pressures (90−125 bar) and an excess of CO_2 relative to H_2 (CO_2:H_2 = 1.5:1 to 3:1).[17−19] Thus, it was necessary to establish that they would operate effectively under the optimal conditions for ester hydrogenation (30 bar H_2/10 bar CO_2). As shown in Table 2, under neutral thermal esterification conditions (0.0126 mmol of catalyst **A** in 2 mL of CH_3OH, 135 °C, 16 h), catalysts **A-1**−**A-3** formed modest quantities of HCO_2CH_3 (entries 1−3). The turnover numbers (TONs) in these systems could be improved by the addition of triethylamine, a base that is commonly used to provide a thermodynamic driving force for the first step of the hydrogenation/esterification sequence (entries 4−6).[17−19] Catalysts **A-2** and **A-3** performed best, providing 21 turnovers after 16 h. However, ester formation was slow under these conditions, and **A-2**/NEt_3 and **A-3**/NEt_3 each afforded only two turnovers after 1 h (Table S3 in the Supporting Information).

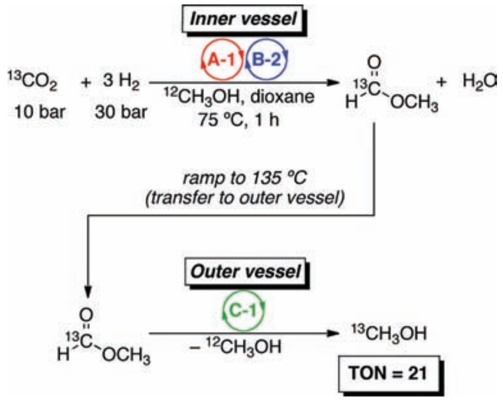
It is well-known that both Brønsted[25] and Lewis acid[26] catalysts can accelerate the esterification of carboxylic acids with alcohols. Thus, we hypothesized that such catalysts might also prove advantageous for the formation HCO_2CH_3 from CO_2. Gratifyingly, the combination of $(PMe_3)_4Ru(Cl)(OAc)$ (**A-1**) and $Sc(OTf)_3$ (**B-2**) provided significantly enhanced TONs of HCO_2CH_3 relative to the thermal and/or base-promoted reactions (TON = 40 vs 3 and 18, respectively; Table 3, entry 4). This **A-1**/**B-2** cascade reaction was also significantly faster than the NEt_3-promoted esterification, with a TON of 32 after 1 h at 135 °C.[27]

With conditions established for steps *a*−*c* at 30 bar H_2/10 bar CO_2, we next examined combining the catalysts to achieve the desired cascade catalytic reduction of CO_2 to MeOH. A variety of **A**/**B**/**C** catalyst combinations were examined (see Table S4 in the Supporting Information) under the following conditions: 30 bar CO_2/10 bar H_2, 0.0126 mmol of each of the catalysts **A**, **B**, and **C**, and 2 mL of CD_3OH. We were pleased to find that the use of **A-1**/**B-2**/**C-1** afforded 2.5 turnovers of CH_3OH along with 34 turnovers of HCO_2CH_3 (Scheme 2). This result provides a proof-of-principle demonstration of the viability of cascade catalysis for effecting this transformation. However, the yield of CH_3OH was significantly lower than would be expected on the

Scheme 2. Cascade Catalytic Conversion of CO_2 to CH_3OH with Catalysts A-1, B-2, C-1, and CD_3OH



Scheme 3. Transfer Approach to Cascade Catalytic CO_2 Hydrogenation



basis of the data in Tables 1 and 3. A series of control experiments revealed that the major problem for cascade catalysis is the deactivation of catalyst **C-1** by $Sc(OTf)_3$. For example, the **C-1**-catalyzed hydrogenation of HCO_2CH_3 with 5 bar H_2 proceeded in only 32% yield in the presence of 1 mol % $Sc(OTf)_3$ (see Table S7 in the Supporting Information).

As a low-tech solution to this competing decomposition process, we physically separated the cross-reactive catalysts within the high-pressure vessel. Catalysts **A** and **B** were placed in a vial in the center of the vessel, while **C** was placed in the outer well of the Parr reactor (Figure S3). In this scenario, the initially formed methyl formate (bp = 32 °C at STP) should transfer from the inner to the outer vessel and undergo hydrogenation. However, the low volatility of the catalysts should prevent deactivation. As shown in Scheme 3, this sequence was successful, and under optimal conditions it provided 21 turnovers of CH_3OH from $^{13}CO_2$.[28]

In conclusion, this communication has demonstrated the viability of cascade catalysis for the reduction of CO_2 with H_2. This approach offers the distinct advantage that it provides opportunities for detailed analysis of the molecular basis of catalyst incompatibilities, the modes of catalyst decomposition, and the slow step of the sequence. As such, we anticipate that it will enable rational tuning of each of the individual catalysts (**A**−**C**) in order to improve the turnover numbers and turnover frequencies for this process. Efforts in all these areas are currently underway in our group and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and representative NMR spectra for the characterization of CO_2 reduction products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
mssanfor@umich.edu

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(28) See Table S5 in the Supporting Information for details.