

Catalytic Synthesis of Acetic Acid from Methanol Using Formic Acid as a Renewable CO Source

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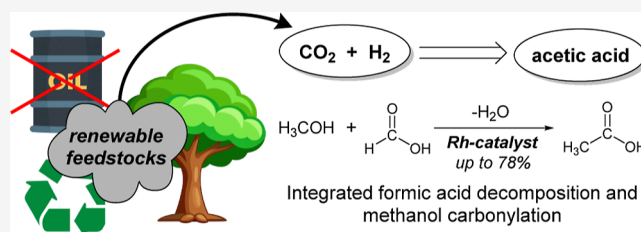
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ABSTRACT: A fully “defossilized” synthetic pathway using green methanol and CO₂-based CO was developed for the production of acetic acid. A catalytic system consisting of [Rh(acac)(CO)₂], PPh₃, and CHI₃ enables integrated formic acid decarbonylation and in situ methanol carbonylation without significant formation of methane. Optimization of the individual components of the catalytic system and their interplay with reaction conditions by design of experiments using a factorial approach resulted in an acetate yield of 78 ± 0.5% in the liquid phase (TON = 960, TOF_{av} = 60 h⁻¹) while maintaining a high CO selectivity of 85 ± 3% in the gas phase.



1. INTRODUCTION

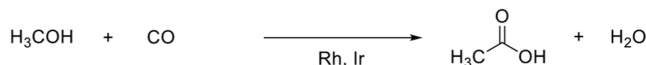
Carbon monoxide defines a pivotal molecular interface at the energy-chemistry nexus. In addition to its use in combination with hydrogen as “syngas” for fuel production, it finds ubiquitous use as a high-energy C-1 building block in industrial chemistry. The largest volume application is the production of acetic acid from catalytic carbonylation of methanol with a ca. 16.1 Mt/a worldwide capacity in 2020, which is forecasted to grow even further to 19.6 Mt/a by 2027.¹ At present, CO is produced mainly by steam reforming from the fossil resources coal, oil, or natural gas. In the context of “defossilization” of the chemical value chain, there are extensive efforts worldwide to utilize CO₂ as a source for CO.^{2–10}

Today, the widely used Monsanto process for the carbonylation of methanol uses a Rh-based catalytic system under operating conditions of 30–40 bar and 180–220 °C.^{11,12} The reaction mechanism is well understood, with methyl iodide undergoing oxidative addition at the active species *cis*-[Rh(CO)₂I₂][−], leading to [Rh(CH₃)(CO)₂I₃][−], which, after migratory insertion of one carbonyl ligand and coordination of another CO, affords acetyl iodide through reductive elimination. Hydrolysis of acetyl iodide yields acetic acid and HI, and the latter reacts with methanol to regenerate methyl iodide.^{12,13} Following a similar mechanism, BP Chemicals developed iridium catalysts in the early 1990s and commercialized the so-called Cativa process in 1995.^{12,14}

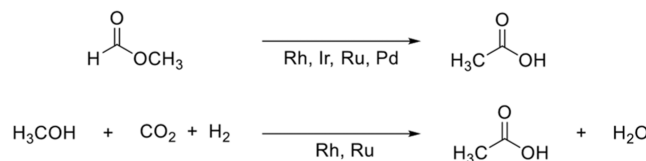
With methanol becoming increasingly available from renewable resources, a combination with CO₂-based CO would open a fully defossilized path to acetic acid. A possible approach in this direction can envisage formic acid (HCOOH, FA) as a CO surrogate (Scheme 1). The mutual interconversion of CO₂/H₂–HCOOH–CO/H₂O has been

Scheme 1. Synthesis of Acetic Acid via Today's Fossil-Based Methanol Carbonylation and Alternative Defossilized Pathways

Fossil-based:



Alternative Pathways:



This work:



non-fossil feedstocks, no esterification step, no methanation

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termed the “formic acid triangle”, circumventing the energy-demanding reverse water gas shift (rWGS) process to access CO.^{15a} Furthermore, liquid HCOOH can be transported and handled more safely than gaseous and toxic CO.

Similar advances have also been made in the field of CO₂ reduction as production routes to formic acid. While direct hydrogenation employing molecular H₂ has already reached high technical maturity,^{18a,16a} recent reports have shown that utilizing biomass-derived reductants such as glucose or lignin may also be envisaged.¹⁷

The decomposition of FA can lead to either CO₂ and H₂ (decarboxylation) or CO and H₂O (decarbonylation). Decarboxylation, which is thermodynamically favored,^{15a} has been investigated extensively regarding its potential use in the hydrogen economy.¹⁸ Decarbonylation has been reported to proceed through strong Brønsted acid catalysis,^{16b} transition metal catalysis,^{16a,19} and base-catalyzed following a chemical looping strategy to suppress the competing decarboxylation reaction.^{16c} Closely related to the transition metal-catalyzed decarbonylation of FA is the water–gas shift equilibrium or (r)WGS reaction. It is well known to be catalyzed by molecular carbonyl halide transition metal complexes, particularly the iodide ones of rhodium²⁰ and ruthenium.²¹ Rh- and Ir-based complexes have previously also been successfully applied in the hydroxycarbonylation of alcohols and olefins to carboxylic acids using formic acid as a CO source in the early 2000s by Simonato.¹⁹

A known approach for acetic acid synthesis using formate as a CO surrogate is the formal isomerization of methyl formate (MF). Many different catalytic systems operating under various conditions have been applied in this reaction, as studied by Bryant,²² Schreck,²³ Cheong and Kang,²⁴ Mortreux and Petit,²⁵ Pruett and Kacmarcik,²⁶ and also by our team more recently.²⁷ Carbonylation of alcohols to carboxylic acids using CO₂/H₂ has been reported by the group of Han²⁸ and our team.^{29,30} For longer-chain alcohols C2+, a Monsanto-type catalytic system based on rhodium proved to be highly efficient. However, yields of acetic acid from methanol remained limited because the presence of H₂ deviated the reaction toward formation of methane as the main product.³⁰ Other, heterogeneously catalyzed approaches toward C1, C2, and C2+ carboxylic acid production include the direct³¹ and indirect³² hydrogenation of CO₂.

Inspired by the studies mentioned above, we sought to develop a strategy to produce acetic acid directly from a mixture of methanol and formic acid. This would make the additional esterification step to MF obsolete and avoid competition with hydrogenation observed with CO₂/H₂. We report here the Rh-catalyzed synthesis of acetic acid from methanol and formic acid, with acetate yields reaching up to 78%, successfully circumventing the aforementioned competing side reaction of methanation.³⁰

2. EXPERIMENTAL SECTION

All relevant information regarding materials and methods is summarized in the Supporting Information. Details about experimental procedures, results, analysis, as well as statistical experiment planning and evaluation are included there, alongside a description of the used equipment.

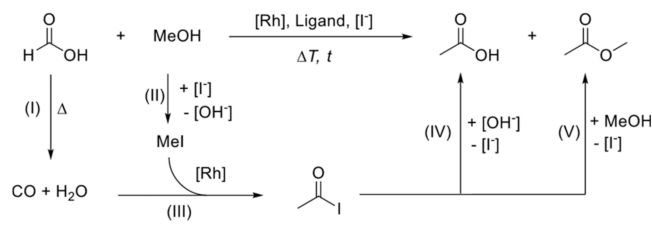
In brief, a high-pressure reactor (10 mL volume) made of Hastelloy C-276 equipped with a digital pressure transducer, a glass inlet, and an oven-dried magnetic stir bar was charged with the respective amount of the metal precursor, ligand, and iodide promoter under an argon atmosphere, and appropriate formic acid (1 wt % H₂O) and methanol

were added afterward using a syringe. The autoclave was immediately sealed and heated to the reaction temperature in a preheated aluminum cone. After the desired reaction time, the autoclave was cooled in an ice bath, and the entire gas phase was carefully vented into a gas sampling bag and analyzed with GC-TCD using ethylene as an internal standard. The liquid phase of the reaction was analyzed with ¹H NMR spectroscopy and/or GC-FID using mesitylene as the internal standard.

3. RESULTS AND DISCUSSION

The reaction network to be controlled for the desired integrated one-pot synthesis is depicted in Scheme 2. The

Scheme 2. Reaction Network for the Synthesis of Acetic Acid from Methanol and Formic Acid via Integrated CO Formation and Subsequent Methanol Carbonylation



decarbonylation of formic acid, liberating CO and water (I), and the conversion of methanol into methyl iodide by iodoform as a promoter (II) are mainly thermal steps. Rhodium-catalyzed carbonylation of methyl iodide yields acetyl iodide (III), followed by hydrolysis to afford acetic acid (IV) or, alternatively, reaction with methanol to form methyl acetate (V).

The decomposition of formic acid and its compatibility with the various catalyst components were studied to identify potentially suitable catalytic systems (Table 1; see also Tables S1 and S2). As expected, the thermal decarbonylation of FA starts to proceed at 160 °C with perfect selectivity toward CO, albeit at a relatively slow rate, leading to 28% conversion after

Table 1. Decomposition of Formic Acid (FA) in the Presence of Catalyst Components Based on the Precursor Complexes [Rh(acac) (CO)₂]₂ C1 and [Ir(cod)Cl]₂ C2^a

entry	complex	PPh ₃ (equiv)	CHI ₃ (equiv)	X _{FA} (%)	gas phase	
					CO (%)	CO ₂ (%)
1				28	>99	<1
2 ^b	C1			29	99	1
3 ^b	C2			25	99	1
4 ^b	C1	5		73	9	91
5 ^b	C2	5		74	14	86
6	C1		2.5	44	99	1
7	C2		2.5	54	94	6
8	C1	5	2.5	28	99	1
9 ^b	C2	5	2.5	24	93	7
10 ^c	C1	5	2.5	85	88	12
11 ^c				83	98	2

^aReaction conditions: $n_{\text{Cat}} = 10.0 \mu\text{mol}$ (based on the metal), $V_{\text{FA}} = 2.0 \text{ mL}$, $T = 160 \text{ }^\circ\text{C}$, $t = 16 \text{ h}$. Liquid phase quantified using ¹H NMR spectroscopy with mesitylene as the internal standard. Gas phase quantified using GC-TCD with ethylene as the internal standard.

^bBlack precipitate observed after the reaction. ^c $T = 200 \text{ }^\circ\text{C}$.

Table 2. Parameter Screening for Integrated Formic Acid Decarbonylation and Methanol Carbonylation^a

entry	PPh ₃ (equiv)	CHI ₃ (equiv)	T (°C)	X _{MeOH} (%)	products			gas phase		
					AcOH (%)	AcOMe (%)	MF (%)	CO (%)	CO ₂ (%)	CH ₄ (%)
1		2.5	160	97	<1	<1	92	n.m.	n.m.	n.m.
2 ^b	2.5	2.5	160	97	2	1	85	n.m.	n.m.	n.m.
3	5.0	2.5	160	98	9	3	80	15	52	34
4	10.0	2.5	160	98	15	4	67	n.m.	n.m.	n.m.
5	20.0	2.5	160	99	12	3	54	n.m.	n.m.	n.m.
6	5.0	10.0	160	98	7	2	74	n.m.	n.m.	n.m.
7 ^b	5.0	25.0	160	98	3	1	68	n.m.	n.m.	n.m.
8 ^b	5.0	2.5	200	98	20	5	50	47	43	9
9 ^b	10.0	2.5	200	78	4	17	5	9	90	1

^aReaction conditions: $n_{C1} = 10.0 \mu\text{mol}$, $V_{FA} = 1.5 \text{ mL}$ (39.4 mmol), $V_{MeOH} = 0.5 \text{ mL}$ (12.3 mmol), $t = 16 \text{ h}$. Liquid phase quantified using GC-FID with mesitylene as the internal standard. Gas phase quantified using GC-TCD with ethylene as the internal standard. ^bBlack precipitate observed after the reaction. n.m. (not measurable): not enough pressure for gas analysis.

16 h (entry 1). At 200 °C, the reaction is substantially faster while largely maintaining the selectivity toward CO (entry 11).

Decarbonylation is not affected by the presence of either [Rh(acac)(CO)₂]**C1** or [Ir(cod)Cl]₂**C2** at 160 °C (entries 2–3). Precipitates of metal black were observed at the end of the reaction, indicating decomposition of the complexes. Addition of five equivalents of ligand PPh₃ per metal center changed the outcome of the reaction markedly, however (entries 4–5). A substantially increased FA conversion was observed, accompanied by a change in selectivity toward the undesired dehydrogenation product CO₂. The catalytic activity of Rh(I)- and Ir(I)-phosphine complexes for the dehydrogenation of formic acid is well documented in the literature, implying that similar species are responsible for the change of the decomposition pathway here.^{15a–c,33–35} The complexes were not stable, and again, metal black was present at the end of the reaction.

Conversely, the addition of the promoter CHI₃ had a positive effect on FA conversion without negatively affecting the selectivity to CO (entries 2–3 vs 6–7). At the same time, it suppressed the catalyst degradation to metal black. Most importantly, the thermal decomposition of FA to yield CO and H₂O remained the predominant pathway when both additives PPh₃ and CHI₃ were present (entries 8–9). This can be rationalized by the oxidative addition of the carbon-iodide bond in the promoter to the low-valent metal centers, leading to Rh(III) and Ir(III) complexes that are largely inactive for formic acid dehydrogenation and more stable.

As slightly higher CO production was observed with the rhodium catalyst based on precursor **C1**, this system was chosen for subsequent experiments. Increasing the temperature to 200 °C, the FA conversion could be significantly enhanced to 85% with only slightly lower CO selectivity of 88% as compared to the absence of the catalyst (entries 10 and 11 and Table S2). The rapid increase of the total pressure and the higher final pressure in the presence of the Rh/PPh₃/CHI₃ system is in line with a substantial contribution of the dehydrogenation pathway (see Figure S1).

The integrated methanol carbonylation with CO generated by formic acid decomposition was targeted with Rh precursor **C1** by varying the ligand- and promoter-to-metal ratios as well as the temperature using a one-factor-at-a-time (OFAT) method for parameter screening (Table 2). MeOH was nearly quantitatively consumed in all experiments. In the absence of PPh₃, the nonproductive esterification of methanol and formic acid to give MF was the dominating reaction, and only traces

of AcOH were observed (entry 1). This implies that FA esterification is faster than its decomposition in the absence of a ligand. Upon addition of 5 equiv of PPh₃, MF formation was reduced and small but measurable amounts of acetic acid were detected (entry 3). However, analysis of the gas phase showed that significant amounts of formic acid were decomposed to CO₂ and H₂, leading to concomitant formation of mostly methane as an undesired product from methanol. Further increase of the PPh₃/Rh ratio resulted in a steady decrease of MF formation, but acetic acid yield remained limited, reaching a maximum of only 15% for the free acid and an additional 4% for its methyl ester at a 10:1 ratio (entries 3–5). An increase of the amount of iodoform to 10:1 and 25:1 ratios per Rh did not improve the acetic acid yield (cf. entries 3, 6, and 7).

At 200 °C under otherwise identical conditions as in entry 3 (5.0 equiv of PPh₃ and 2.5 equiv of CHI₃), the total acetate content increased to 25%, while the MF fraction dropped to 50% (entry 8). The improved acetate production is in line with the much higher CO production rate observed at this temperature (Table 1, entry 10). The gas-phase composition shows that a significant amount of CO is present at the end of the reaction. The pathway to CO₂ and H₂ is still very significant, but methane formation is less pronounced. Doubling the ligand amount to 10 equiv led to roughly the same amount of carbonylation reactivity, but methyl acetate was the major product in this case (entry 9). Almost no MF was formed (5%), and large amounts of CO₂ (90% share in the gas phase) indicate that FA decarboxylation took place to a large extent. It should be noted that the quantification of products in the used procedure showed a significant gap at 200 °C, indicating additional possible decomposition processes for methanol and methyl intermediates.

In line with the results from the carbonylation of long-chain alcohols with CO₂/H₂,^{29,30} some qualitative conclusions can be drawn from the data in Table 2 and further variations (Tables S3 and S4). First, it is important to avoid the extensive formation of MF, as the ester is largely unreactive for carbonylation with the rhodium-based catalysts (see Table S8). Second, the ratio of PPh₃/Rh must be in a narrow range in order to achieve carbonylation and at the same time avoid extensive FA decomposition to CO₂ and H₂. Third, the ratio of CHI₃/Rh has less of a direct impact but affects the PPh₃/Rh ratio due to quaternization of the phosphine ligand. As many of the involved interconversions are equilibrium reactions, the absolute amounts of the liquid substrates influencing the concentrations add further to the complexity.

The individual variation of these intertwined and partially contradictory requirements by OFAT-type experiments is obviously not sufficient to optimize the catalyst system. Therefore, we turned toward a design of experiments (DoE) approach.³⁶ First, a factorial design and analysis was conducted for six selected parameters deemed most influential on the system (see Table S5), including the temperature, volumes of FA and MeOH, the amounts of iodoform and C1, as well as the PPh₃/C1 ratio. The results of these experiments can be found in Table S6 and Figures S2 and S3. The most influential—singular or isolated—parameters on the acetate formation were found to be V_{MeOH} , $n_{\text{CH}_3\text{I}}$, and n_{C1} , whereas gas-phase CO selectivity is influenced the strongest by the temperature and V_{FA} . In the latter case, increasing the respective parameter shows a positive influence, and with regard to acetate formation, V_{MeOH} and n_{C1} appear to have a strong negative impact, whereas an increased iodoform amount seems beneficial.

The data from the statistical planning indicated that the many interwoven activation and deactivation processes of the system prevent optimization of individual aspects for parameter/performance correlations. Regardless, the DoE approach narrowed the relevant parameters for the final system optimization, thus decreasing both the complexity and number of experiments necessary to obtain valuable results. The temperature was set consistently to 200 °C, and the FA and MeOH volumes were fixed to a high and low amount, respectively, benefiting both the acetate formation and the CO selectivity. The parameters to be optimized within the predetermined ranges were the amount of rhodium precursor C1, the ratio of triphenylphosphine to the rhodium precursor, and the amount of the iodoform promoter (see Table 3).

Table 3. Factor and Level for the Optimization Using the Response Surface Methodology (RSM)

factor	unit	level		
		−1	0	+1
A: n_{C1}	μmol	1.0	5.5	10
B: PPh ₃ /C1		3.0	11.5	20
C: $n_{\text{CH}_3\text{I}}$	μmol	100	175	250

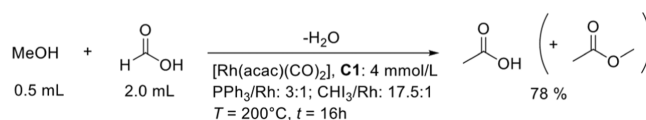
Acetate formation was set as the target parameter as it is considered more important than the CO selectivity in the gas

phase. The experiments and results are summarized in Table S7.

Analysis of the results was performed by applying the RSM after Box and Behnken³⁶ and is graphically displayed in Figure 1. The results quantitatively confirm that a high n_{C1} combined with a low PPh₃/C1 ratio is favorable for acetate formation, while $n_{\text{CH}_3\text{I}}$ appears to be of lesser significance compared to the other two parameters for the investigated range. The analysis demonstrated the possibility of high efficacy for the integrated decomposition and carbonylation reaction, with the total yield of acetic acid and methyl acetate approaching 80%.

The conditions identified for optimum acetate yield (Table S7, entry 2; Scheme 3) were validated in a repeated

Scheme 3. Rhodium-Catalyzed Synthesis of Acetic Acid from Methanol and Formic Acid under DoE-Optimized Conditions



independent experiment, confirming an acetate fraction in the liquid phase of 78 ± 0.5 consistently at a CO selectivity in the gas phase of $85 \pm 3\%$. The data correspond to a turnover number for acetate formation, TON, of around 960 for productivity, and a turnover frequency, an average over the whole reaction time, TOF_{av}, of 60 h^{-1} as a lower limit for activity.

Based on the experimental results obtained in this study and previous works,^{28–30} a basic mechanistic picture can be proposed for the integrated overall transformation of methanol carbonylation with CO generated from in situ formic acid decarbonylation (Scheme 4). The formic acid decarbonylation, which may occur thermally or partially also catalytically, has to be favored over the competing catalytic decarboxylation. The generated CO will be consumed in the second cycle via carbonylation of methanol following a typical Monsanto-type mechanism. Iodoform acts as a promoter to activate the methanol in the form of methyl iodide in situ, avoiding the use of toxic methyl iodide as a separate additive.

4. CONCLUSIONS

In conclusion, integrated formic acid decomposition and carbonylation of methanol open a fully “defossilized” pathway

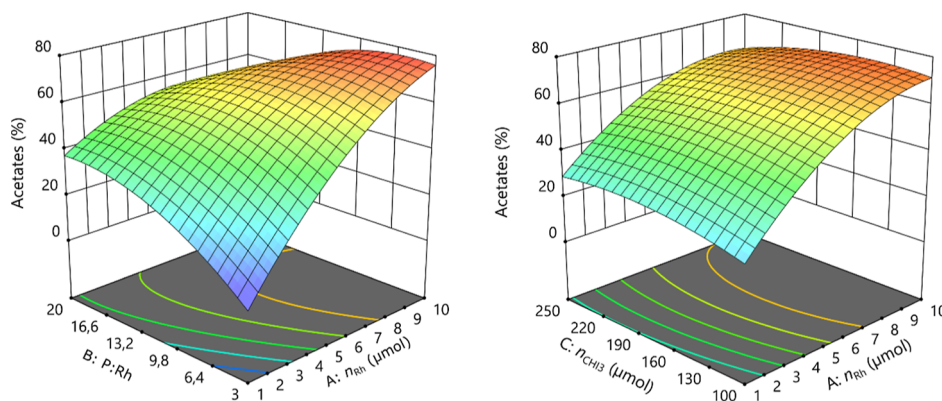
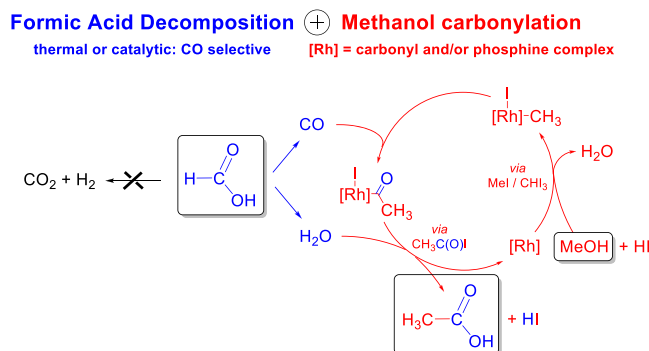


Figure 1. RSM graphs for the response acetates as retrieved from the experimental plan. Factors are A: n_{Rh} , B: P/Rh, and C: $n_{\text{CH}_3\text{I}}$.

Scheme 4. Proposed Mechanistic Pathway of Coupled Formic Acid Decarbonylation and Methanol Carbonylation Catalyzed by Molecular Rh Complexes (cf. Scheme 3 in ref 29 for CO₂/H₂-Based Systems; Adapted with Permission from ref 29. Copyright 2013 Wiley-VCH/John Wiley and Sons. License Number: 6135321425613)



to acetic acid. Formic acid provides a CO surrogate that can be obtained from CO₂ via catalytic hydrogenation.^{2,3,15a} In addition, electrochemical, photochemical, and biological processes to formic acid from CO₂ are also well investigated.^{37–41} Furthermore, production of formic acid from lignocellulosic biomass provides another nonfossil access to this CO carrier.^{42,43}

The key challenge for the development of effective catalytic systems for this process lies in the judicious control of a complex network of thermal and catalytic reaction steps. In the present study, it was demonstrated that a rhodium-based catalytic system involving PPh₃ as a ligand and CHI₃ as an iodide promoter withstands and is active during the thermal decarbonylation of formic acid to generate CO while effectively catalyzing methanol carbonylation to acetic acid. Whereas separate variation of individual parameters proved insufficient to optimize the complex system, statistical DoE planning allowed the identification of a suitable ratio of the catalyst components and reaction conditions. Thus, the fraction of acetic acid and its methyl ester in the liquid phase could be optimized from initially 2% to 78%, demonstrating the power of the approach. Under optimized conditions, the production of acetate corresponded to a TON of 960 and TOF_{av} = 60 h^{−1} per rhodium. Further studies aiming at recycling of the complex catalytic system or even continuous operation of the reaction would seem promising to further optimize the reaction for practical use.

In general, the results of the present study provide a further example of the strategic use of the “formic acid triangle” CO₂/H₂–HCOOH–CO/H₂O for the defossilization of chemical production.^{2,15a} Given the numerous catalytic systems known to adjust the necessary equilibria and to catalyze carbonylation reactions, further opportunities for CO₂ capture and conversion may arise at the interface of energy and chemistry.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.5c04169>.

General information regarding experiments, methods, and materials including thermal decomposition of FA in the presence and absence of the Rh-based catalytic system (Table S1); pressure–time diagrams of the

thermal decomposition of FA in the presence and absence of the Rh-based catalytic system (Figure S1); influence of temperature on the decomposition of FA using the Rh-based catalytic system (Table S2); influence of temperature and the catalyst precursor on the carbonylation of methanol with FA (Table S3); influence of the iodine promoter and phosphine ligand and other additives on the carbonylation of methanol using FA (Table S4); parameters chosen for factorial design optimization of the Rh-catalyzed carbonylation of methanol using FA (Table S5); half-normal and Pareto plots for acetate production (Figure S2) and for CO formation (Figure S3); experimental results for the Rh-catalyzed carbonylation of methanol using FA based on a factorial design approach (Table S6) and based on the response surface methodology (Table S7); isomerization and gas generation of methyl formate under catalytic methanol carbonylation conditions (Table S8); schematic representation and detailed description of the experimental setup (Figure S4); and representative analytical data (Figures S5–S7) (PDF)

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Author Contributions

[§]P.J.-W. and N.J.L. contributed equally to this work. N.J.L. carried out most of the catalytic experiments and sample preparations, and analysis as part of their bachelor's thesis. P.J.-W. planned the experiments and performed all of the analysis regarding statistical experimental planning (DoE methodology) and the optimizations applying the factorial design and response surface methodologies. G.F. and W.L. conceived and supervised the project. N.J.L. and W.L. wrote the manuscript.

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Notes

The authors declare no competing financial interest.

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