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Aqueous Biphasic Systems for the Synthesis of Formates via Catalytic CO₂-Hydrogenation: Integrated Reaction and Catalyst Separation for CO₂-Scrubbing Solutions

Martin Scott, Beatriz Blas Molinos, Christian Westhues, Giancarlo Franciò* and Walter Leitner*

Dedicated to Prof. A. Behr on the occasion of his retirement acknowledging his pioneering contributions on the use of CO₂ as C1 building block

Abstract: Aqueous biphasic systems were investigated for the production of formate-amine-adducts via metal-catalyzed CO₂hydrogenation. Different hydrophobic organic solvents and ionic liquids could be employed as the stationary phase for cis-Ru(dppm)₂Cl₂ as prototypical catalyst without any modification or tagging of the complex. The solvent pair methyl-isobutylcarbinol (MIBC) and water led to the most practical and productive system and repetitive use of the catalyst phase was demonstrated achieving high endurance with a total TON 150.000 and high activity with a TOF_{av} of ca. 35.000 h⁻¹ and an initial TOF of ca. 180.000 h⁻¹. Whereas the partitioning of the amines between the two phases was found to vary depending on their structures, the generated formate-amine-adducts were quantitatively extracted into water phase in all cases. Remarkably, the highest productivity were obtained with methyldiethanolamine (Aminosol CST 115®) and monoethanolamine (MEA), which are used in commercial scale CO2scrubbing processes. Saturated aqueous solutions (CO2 overpressure 5-10 bar) of MEA could be converted to the corresponding formate adducts with average turnover frequencies up to $14 \times 10^5 h^{-1}$ with an overall yield of 70% based on the amine amount corresponding to a total turnover number of 150 000 over eleven recycling experiments. This opens the possibility for integrated approaches to carbon capture and utilization.

Introduction: The increased interest in closed carbon cycles across different industrial sectors results in renewed strong impulses toward investigations of the use of carbon dioxide as a chemical feedstock.^[1] The physico-chemical properties and nontoxicity of CO₂ together with its abundant availability at highly concentrated point sources endorse its potential application as C1 building block.^[2] In particular, the hydrogenation of carbon dioxide into formic acid and formate adducts has been widely studied^{[3],[4]} because of their broad industrial use as biomass preservative,[5] in the textile industry,[5] as additive for pharmaceuticals and food,^[5] and possible future opportunities as hydrogen storage materials^[6] or as safe CO and phosgene substitutes.^[7] During the last decades, very potent homogeneous^[8] Rh-,^[9] Ru-,^[10] Ir-,^[11] Fe-^[12] or Co^[13]-based catalytic systems have been developed for this transformation. However, the next crucial steps toward the applications of such systems - namely the integration into CO₂-based value chains with separation and recycling of the homogenous catalyst -

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Due to the interplay of thermodynamic and kinetic boundary conditions for the transformation of CO_2 and H_2 into formic acid, the catalytic system comprising the molecular active species and the reaction medium has to be carefully and systematically adjusted for the targeted applications. In this context, aqueous biphasic systems seem particularly attractive as aqueous amine solutions are used on commercial scale as CO_2 -scrubbing media. At the same time, they offer the potential to separate or immobilize the organometallic active species if combined with hydrophobic solvents as catalyst phase. To the best of our knowledge, however, the application of industrially used scrubbing amines in biphasic aqueous systems with *in situ* catalyst removal has not been demonstrated yet.

Already in 1989, BP chemicals described in a patent a biphasic system comprising aliphatic or aromatic hydrocarbons as catalyst phase and alcohols or water as the product phase for HCOOH adducts with trialkylamines such as $\mathsf{NEt}_3.^{[14b,\ 14c]}$ The catalyst solution was re-used three times, but very low turnover numbers (TON) in the range of 150-190 were obtained in each cycle. In 2003, the group of Laurenczy reported a high pressure NMR study on the hydrogenation of aqueous bicarbonate solutions in a biphasic system comprising water immiscible ILs as catalyst phase.^[14g] A maximum turnover frequency (TOF) of 450 h⁻¹ was observed, but no attempts to recycle the catalyst were reported. More recently, Schaub and Paciello at BASF reported a highly productive biphasic system composed of an apolar tertiary amine such as NHex₃ and polar high boiling diols.^[14d,14e] The catalyst was largely retained in the excess amine and separated from the polar product phase by backextraction with the same amine.

Another line of research focused on homogeneous single phase aqueous systems employing water soluble catalysts and amines. In 1993, our group reported the first hydrogenation of CO₂ to formate in aqueous amine solutions using a water Wilkinson-type catalyst.^[16] This approach soluble was successfully extended to solutions comprising the ethanol amines used in commercial scale CO2-scrubbing processes as bases.^[17] Although a variety of catalysts have been described since then for CO₂ hydrogenation in aqueous solutions using amines or inorganic bases,^[18] and even under base-free conditions,^[19] this early work appears to be still the only study employing commercially relevant scrubbing amines. While the present manuscript was in preparation, a paper by Olah and Prakash was published discussing also the concept of using amine-based aqueous CO2-scrubbing solutions in combination with an organic catalyst phase. Total TONs of up to 7000 and maximum TOFs of 600 h⁻¹ were reported, albeit with amines that are not applied in flue gas separation.[20]

We present here a detailed study on the hydrogenation of CO₂ in biphasic systems comprising hydrophobic solvents as catalyst immobilization phases and water as a product extraction phase.^[21] Different ILs and organic solvents have been evaluated focusing on productivity and integrated catalyst separation for variety of amines including а methyldiethanolamine (Aminosol CST 115[®]) and monoethanolamine (MEA) as prototypical scrubbing amines (Figure 1). Importantly, this immobilization strategy does not require any modification or tagging of the ligand/catalyst and an established Ru-catalyst was used to validate this approach. High catalyst activity and stability were observed for a range of amines and semi-continuous operation was successfully implemented with saturated mono-ethanolamine solutions of CO₂ as feedstock, demonstrating the potential integration with carbon capture technologies.



Figure 1. Schematic display of the investigated systems a) ionic liquid/water (upper scheme); b) organic solvent/water (bottom scheme).

Results and Discussion

The complex *cis*-Ru(dppm)₂Cl₂ (dppm = bis-diphenylphosphinomethane) $1^{[23]}$ was used as catalyst precursor throughout the present study. It was synthesized by adapting literature known procedures^[24] as shown in Scheme 1. Pre-catalyst 1 was chosen due to the known efficacy of Ru-phosphine complexes for CO₂ hydrogenation under a broad range of reaction conditions and in various solvent systems.^[4i] Complex 1 also shows solubility in a broad range of solvents from medium to low polarity, making in particularly attractive for the envisaged biphasic systems.



As a first approach, the combination of hydrophilic ionic liquids (ILs) and water was investigated. Preliminary CO_2 hydrogenation experiments in IL/H₂O in the presence of an amine showed that

significant extraction of imidazolium formate into the water phase occurred when [EMIM][NTf₂] was used as the catalyst phase. In contrast, the more hydrophobic IL [OMIM][NTf₂] with a long alkyl chain did not show any cation leaching into the aqueous phase and was therefore selected as the catalyst phase. The secondary dimethylamine and diisopropylamine as well as the tertiary triethylamine were selected to represent both hydrophilic and hydrophobic amines. NEt₃ is widely employed as benchmark in catalytic CO₂ hydrogenation allowing for comparison with previously reported single phase systems.^[22] Partitioning experiments were carried out to evaluate the solubility behavior of the amines and their corresponding formate adducts in the biphasic medium (table 1).

Table 1. Partitioning of different amines and the corresponding formate adducts in H_2O/[OMIM][NTf_2]^{[a]}

Amine	free amine in H ₂ O phase	free amine in IL phase	formate-amine adduct in H ₂ O phase
HNMe ₂	56%	44%	>95%
HN′Pr ₂	23%	77%	>95%
NEt ₃	7%	93%	>95%

^[a] Determinations via ¹H NMR (accuracy ±5%), see SI for details.

As expected, the amines partition more readily in the aqueous phase accordingly to their polarity. Importantly, the corresponding formate-amine adducts reside almost exclusively in the water phase irrespective of the amine's partitioning. This phase behavior appears beneficial for the envisaged integrated reaction/separation sequence as the amine has a significant initial concentration in the catalyst phase whereas the product is effectively removed into the aqueous phase.

Hydrogenation reactions in the IL/H₂O system were carried out in a window autoclave with 30 bar CO₂ and 60 bar H₂ for a total pressure of 90 bar (at r.t.) at two different loadings (0.05 and 0.13 mol%). For a direct comparison of the examined amines, all reactions were performed at 70 °C providing sufficiently high reaction rates for all systems. At higher temperatures the formate adduct of dimethylamine undergoes dehydration and formation of dimetylformamide. The reaction progress was followed by monitoring the pressure drop from which an initial turnover frequency TOF_{ini} was calculated (figures S1 and S4). At the end of the reaction, acetone/dmso (1:1, v/v) was added to the biphasic system thereby obtaining a single phase, which was analyzed by ¹H-NMR using cyclohexene or mesitylene as internal standard and a pulse delay of 20 s. The accuracy of this method was calibrated using HCOOH/amine standard solutions and deviations of ±5% were found. No signals indicating amide formation were detected and maximum HCOOH-to-amine ratios of up to 1:1 were observed in accord with the limiting conversion already shown in previous studies using single-phase aqueous media.^[16,17] In comparison, water-free systems show higher HCOOH to amine ratios of up to 1.6:1.[10c]

High CO₂ conversions to formic acid corresponding to 84%-97% of the initial amine amount were obtained with all three tested amines. Dimethylamine led to the most rapid CO₂ conversion in the biphasic system IL/H₂O and a TOF_{ini} of about 5000 h⁻¹ was achieved independently from the catalyst loading used (Table 2,

entries 1 and 2). This indicates that no mass transfer limitations are occurring under these conditions despite the fact that this amine showed the most unfavorable partition coefficient residing prevalently in the water and not in the catalyst phase. Lower reaction rates were observed with $HN'Pr_2$ and NEt_3 (Table 2 entries 3-6). Higher values of TOF_{ini} were obtained with both amines at higher catalyst loading possibly indicating some catalyst deactivation at lower catalyst concentration.

Table 2. Ru-catalysed hydrogenation of CO_2 in the presence of different amines in the biphasic system [OMIM][NTf_2]/H_2O.^{[a]}

	CO ₂ +	H ₂ cis	-Ru(dppm	h) ₂ Cl ₂ HCC	DOH/amir	ne
#	amine	Cat. ^[b] [mol%]	t [min]	HCOOH/amine [mol/mol]	TON	TOF _{ini} [c] [h ⁻¹]
1	HNMe ₂	0.05	53	n.d. ^[d]	1875	5340
2	HNMe ₂	0.13	20	n.d. ^[d]	690	5060
3	HN′́Pr₂	0.05	316	96/100	1720	300
4	HN′́Pr₂	0.13	63	91/100	690	1080
5	NEt ₃	0.05	212	95/100	1615	740
6	NEt ₃	0.13	50	92/100	690	2040

[a] reaction conditions: 10 mL window autoclave, amine (~7.9 mmol), IL (ca. 1 mL), H₂O (1.5-1.7 mL), total pressure = 90 bar (60 bar H₂, 30 bar CO₂, pressurised at r.t.), 70 °C, vigorous stirring; [b] based on amine loading; [c] calculated from pressure-time profiles: see SI for complete data; [d] The signal of acetone used for the homogenization of the two phases overlaps with that of the methyl groups of dimethylamine hindering the determination of the HCOOH/HNMe₂ ratio for this amine.

The suitability of the biphasic catalytic system for catalyst separation and reutilization was then investigated using dimethylamine as the base. After the first experiment, the reactor was cooled down to r.t. and most of the aqueous phase containing the formate adduct was carefully removed with a syringe under inert atmosphere leaving the catalyst phase in the reactor. Hereby a thin aqueous layer (~0.5 mL) was left on top of the IL phase to ensure that no catalyst phase was inadvertently removed. The formate concentration in the isolated aqueous solutions was quantified by ¹H-NMR spectroscopy using 1,4-dioxane or sodium benzoate as internal standard. The autoclave was then refilled with a fresh aqueous solution of dimethylamine and the reactor pressurized again with CO_2/H_2 and heated to $70^{\circ}C.^{[25]}$ The pressure-time curves of four consecutive experiments are shown in Figure 2.

This procedure allowed an effective recycling of the IL-phase, but the reaction rate after each run decreased significantly indicating some catalyst deactivation. A total TON (TTON) of 6550 was determined from the analysis of the combined reaction solutions over four reactions corresponding to an overall yield of 87% in the isolated aqueous phase based on the initial amine amount (see SI, table S2). This is comparable with the single run experiments reported above (cf. table 2, entry 1 and 2). Aliquots

of the product phase from each experiment were submitted to ICP-MS. Whereas the Ru-leaching was very low ranging between 0.3-0.8% pro run, the P-leaching was more pronounced with values ranging from 1.2-2.3% pro run with a total loss over the four runs of the initially charged catalyst of 2.2% and 7.0% for ruthenium and phosphorus, respectively, indicating a certain degree of catalyst decomposition (see SI table S3).



Figure 2. Pressure-time curves for the CO₂ hydrogenation in the biphasic system [OMIM][NTf₂]/H₂O with HNMe₂ as base. Conditions: 20 mL window autoclave, HNMe₂ (15.8 mmol), 1 (7.8 mg, 0.08 mmol corresponding to 0.05 mol% of amine used in the first run), IL (ca. 2 mL), H₂O (3 mL), 90 bar total pressure (60 bar H₂, 30 bar CO₂, pressurised at r.t.), 70 °C, vigorous stirring.

Since the IL-based biphasic system demonstrated the principle feasibility of the approach but showed with limited stability we turned our interest to organic/H2O-systems. Various water immiscible solvents with quite different physico-chemical properties were evaluated. Toluene, already used in the BPsystem^[14b,14c] was included as representative low-polarity solvent, while bio-based 2-methyltetrahydrofuran (2-MTHF)[26] and cyclopentyl-methylether (CPME)[27] were selected as water immiscible ethers with moderate polarity. The cheap and readily available alcohol methylisobutylcarbinol (MIBC) was chosen as protic yet water immiscible polar solvent.^[28] All these solvents are regarded as industrially acceptable according to the solvent selection guidelines.^[29] Dimethylamine, triethylamine and monoethanolamine (MEA), as prototypical example of a scrubbing amine applied on commercial scale,^[30] were used as amine components.

The partitioning of the amines in the different organic/H₂O systems reflects again the amine polarity and increasing preference for the aqueous phase was observed for NEt₃ < MEA < HNMe₂ in all cases. The absolute values obviously correlate with the polarity of the individual organic solvents (see table S1 in SI). Again, the corresponding formate adducts partitioned exclusively in the aqueous phase warranting the pre-requisite for efficient biphasic catalysis and separation.

The hydrogenation reactions were performed under the same conditions as before using a catalyst loading of 0.05 mol% relative to the amine. The benchmark NEt₃ was used as amine and at least three recycling experiments were conducted for evaluating the different organic/H₂O systems (table 3).^[31]

Toluene resulted in the lowest reaction rate of all solvents with only small variations over the three runs (see figure S5 for pressure-time profiles). A total yield of 69% over three runs was achieved (table 3, entry 1). Visual inspection revealed yellow solid material present during the catalysis indicating an insufficient solubility of the catalyst in this medium. This observation may explain the poor performance obtained in the toluene/H₂O system.

An almost ten times faster reaction than in toluene was observed using CPME as catalyst phase (table 3, entry 2) although **1** was again not completely soluble in this medium. A significant decrease of activity was observed after each run leading to an initial gas consumption rate $(\Delta p/\Delta t)$ in the 3rd run of only 28% as compared to the 1st run

(see Figure S6 for pressure-time profiles). An overall yield of 68% in the isolated aqueous solutions over three runs was obtained.

2-MTHF provided good catalyst solubility under the applied reaction conditions and rapid CO₂ hydrogenation was achieved (for pressure-time profiles see Figures S7 and S8). In the first and second run, the catalyst showed a TOF_{ini} of ~11000 h⁻¹ (table 3, entry 3). In the third run, however, the catalyst activity dropped abruptly and the reaction was stopped before full completion was reached.^[32]

Finally, an excellent combination of high activity and endurance was obtained when MIBC was used as catalyst phase (table 3, entry 4-6). In the first run the catalyst showed only moderate activity. After this induction period, however, the system exhibited excellent performance in the second run and the reaction was completed within ~3 minutes with a TOF_{ini} of ca. 180 000 h⁻¹ and a TOF_{av} of ca. 35 000 h⁻¹(Figures 3, S4 and S9).^[33]



Figure 3. Pressure-time profiles (initial 10 bar pressure uptake) for the hydrogenation of CO_2 in the presence of NEt₃ in the biphasic system MIBC/H₂O ((cf. table 3, entry 4; for complete data see SI).

Table 3. Hydrogenation of CO_2 with the different amines in the system organic/H₂O.^[a]

#	solv.	amine	Runs	<i>t</i> ^{(b]} [min]	Yield ^[c] [%]	HCOOH /amine ^[d] [mol/mol]	TTON	TOF _{av} ^[e] [h ⁻¹]	TOF _{ini} ^[e] [h ⁻¹]
1	Toluene	NEt ₃	3	415 ^[f]	69	90/100	4010	262	420 ^[f]
2	CPME	NEt ₃	3	19 ^[g]	68	89/100	3930	3412	4714 ^[g]
3	2-MTHF	NEt ₃	3	14 ^[f]	49	66/100	2980	7300	11200 ^[f]
4	MIBC	NEt ₃	10	3 ^[f]	75	86/100	14540	≥35000	180000 ^[f]
5	MIBC	HNMe ₂	7	7 ^[g]	85	93/100	11430	16500	31400 ^[g]
6	MIBC	MEA	7	10 ^[f]	83	92/100	11340	15200	17300 ^[f]
7	MIBC	Aminosol CST 115 ^{®[h]}	10	12 ^[i]	83	100/100	18170	8109	41000 ^[g]

[a] 10 mL window autoclave, amine (~7.9 mmol), 1 (4.1 μ mol) organic solvent (1.5 mL), H₂O (2 mL), total pressure 90 bar (60 bar H₂, 30 bar CO₂, pressurised at r.t.), 70 °C,(for more time details see SI, table S4), vigorous stirring; [b] time to reach reaction completion (constant pressure) in the given run; [c] overall yield of all runs referred to the amount of amine used and calculated from the formate concentration in each isolated aqueous product phase as quantified by ¹H-NMR; [d] average HCOOH/amine ratio of all runs [e] calculated from pressure-time profiles: see SI for complete data; [f] determined for the second run; [g] determined for the first run; [h] 1:1 (v/v) mixture with water, 9.0 mmol per run, for detailed procedure see SI; [i] average over all runs.

The activity remained high in the third run and the repetitive use was therefore extended. The pressure uptake of each run was monitored and the reaction reached constant pressure within 15 min for the first eight runs.^[33] Catalyst deactivation started to become apparent in the 7th run and the experiment was stopped after the 10th run, when an initial gas consumption rate of only 5% as compared to the 2nd run remained. Thus, a TTON of ~14 500 could be achieved over the 10 runs in the system NEt₃/MIBC/H₂O (table 3; entry 4).

The use of HNMe₂ also led to rapid hydrogenation of CO_2 in the biphasic MIBC/H₂O system. However, loss of catalyst activity was more pronounced with this amine (see Figure S11 and S12). The initial gas consumption rate in the 7th run dropped to 12% as compared the 1st run (see Figure S11 and S12). A TTON of ca. 11 400 was obtained over seven runs (table 3, entry 5; Figure S10 to S12).



Figure 4. Pressure-time profiles for hydrogenation of CO₂ in the presence of MEA in the biphasic system MIBC/H₂O (cf. table 3, entry 6; for complete data see SI)

Gratifyingly, the MIBC/H₂O system proved particularly effective in combination with MEA as amine component (table 3, entry 6). Under standard conditions, excellent activity corresponding to a TOF_{ini} of 17300 h⁻¹ was observed already in the first run, indicating that the formation of the active catalyst species is more rapid in this case. The activity was largely retained upon recycling as judged from the pressure-time profiles (see figures 4, S13 and S14) and 63% of the initial activity was still observed after 7 runs. A TTON of 11300 was achieved at this stage.

Even more stable catalyst performances were observed with the industrially used scrubbing amine solution Aminosol CST $115^{(8)}$ in a 1:1 (v/v) mixture with water (table 3, entry 7). Differently from the other amines, a turbid mixture resembling an emulsion was obtained upon pressurizing the system at room temperature. As the early partial mixing of the aqueous and the catalyst phase does not allow a defined start of the reaction, the stirrer was switched on from the beginning of the heating period taking ca. ~13 minutes to reach the final temperature of 70 °C. A clear phase separation was obtained at the end of the reaction and, thus, allowing facile isolation of the aqueous product phase and recycling of the catalyst phase. High activity corresponding to a TOF_{ini} of 41000 h⁻¹ was observed already in the first run, suggesting that the formation of the active catalyst species is more rapid in this case. More importantly, the activity was almost entirely maintained throughout the recycling experiments as indicated by the pressure-time profiles (figure 5) and a TTON of 18170 was achieved in 10 runs (table S5).



Figure 5. Pressure-time profiles for hydrogenation of CO₂ in the presence of Aminosol CST 115° in the biphasic system MIBC/H₂O (cf. table 3, entry 7; for complete data see SI; the stirrer was switched on already at the beginning of the heating ramp taking ca. 13 minutes)

Determination of Ru- and P-leaching via ICP-MS measurements of the content in the aqueous phase confirmed the efficacy of the biphasic system MIBC/H₂O (table 4). A Ru-leaching ranging from 1.2%-2.9% in each run was found in the recycling experiments carried out in the presence of NEt₃ and HNMe₂ accounting for a total Ru-loss of 9.5% and 10.6% after 5 runs (table 4). Lower P-leaching was found in case of NEt₃ (4.8% total P-loss after 5 runs) compared to HNMe₂ (10.9% total P-loss after 5 runs). Noteworthy, significantly better catalyst retention was achieved in the presence of MEA with leaching values way below 1% per each run. A total P- and Ru-leaching below 2% of the originally loaded catalyst material even after 5 runs was determined via ICP-MS corroborating the high potential of the MIBC/MEA-H₂O system which combines readily available components, high catalyst stability, and low leaching. Very low Ru-leaching of 0.21% per run in average over ten cycles were found also in the presence of Aminosol CST 115[®] whereas Pleaching was significantly higher with an average value of 1.00% per run (cf. table S5). Interestingly, there is no direct correlation between the reaction rate and the leaching data indicating that chemical activation and deactivation of the catalytic species play a major role for the performance in the recycling sequence.

Table 4. Leaching values for the first 5 runs in the MIBC/H ₂ O system (c	;1
Figure 3 for NEt ₃ , cf Figure S11 for HNMe ₂ ,MEA cf Figure 4 for MEA). ^{[a}	1]

						224		
	Bun	N	NEt ₃		HNMe ₂		MEA	
	Run	Ru	Ρ	Ru	Р	Ru	Ρ	
	1	1.30%	1.60%	1.96%	1.97%	0.24%	0.60%	
	2	1.22%	0.72%	1.22%	0.91%	0.17%	0.46%	
	3	2.09%	0.96%	2.09%	1.71%	0.38%	0.26%	
	4	2.90%	0.85%	2.83%	2.54%	<0.01%	0.22%	
K.	5	2.02%	0.67%	2.46%	3.78%	0.52%	0.28%	

^[a] determined via ICP-MS measurement of the concentration in the aqueous product phase and expressed as % of the initial catalyst loading

These very positive results prompt us to study the integrated hydrogenation and product separation with aqueous MEA solutions as used in large scale applications for post-combustion CO_2 -capture.^[30] To this aim, the use of an aqueous solution of MEA at a loading ~20 wt%,^[36] which was pre-saturated with CO_2 at low overpressures, was examined as feedstock for direct hydrogenation (table 5).^[37]

Table 5. Hydrogenation of CO ₂ with MEA in MIBC/H ₂ O ^[a]									
#	<i>p</i> CO₂ [bar]	<i>p</i> H₂ [bar]	p _{total} [bar]	Yield [%]	HCOOH/amine [mol/mol]				
1	2	88	90	59	59/100				
2	5	25	30	56	67/100				
3	5	55	60	74	81/100				
4	5	85	90	80	94/100				
5	15	75	90	73	94/100				

[a] 10 mL window autoclave, amine (~7.9 mmol), 1 (4.1 μ mol) MIBC (1.5 mL), H₂O (2 mL); 70 °C, *t* = 10-15 min (time to constant pressure in the reactor), vigorous stirring; [b] yield referred to the initial amount of amine and calculated from the formate concentration in the isolated aqueous product phase as quantified by ¹H-NMR.

A MEA solution with just 2 bar CO_2 overpressure could be hydrogenated with 59% yield using 88 bar H₂ (table 5, entry 1). The same yield was achieved using slightly higher CO_2 overpressure of 5 bar and much lower H₂ pressure of 25 bar (table 5, entry 2). Increasing the hydrogen pressure to 55 bar led to 74% yield (table 5, entry 3). Virtually full conversion to reach an almost 1:1 HCOOH/amine ratio was achieved with 85 bar H₂ (table 5 entry 4). A similar result could also be obtained at identical total pressure of 90 bar increasing the partial pressure of CO₂ and reducing the pH_2 to 75 bar (table 5 entry 5). These experiments show that saturated MEA-solutions with low CO₂ overpressure can serve directly as feedstock for the hydrogenation of carbon dioxide to yield nearly stoichiometric amounts of formic acid per amine.



Figure 6. Schematic display of the semi-continuous system for the direct hydrogenation of CO_2 -saturated aqueous MEA-solutions.

Finally, the system MIBC/H₂O-MEA was selected for validating this approach under semi-continuous operation.^[38] For these experiments, a 100 mL stainless steel autoclave was used equipped with a mechanical stirrer, an outlet valve at the bottom of the reaction chamber, an inlet valve for delivery of substrate solution via a HPLC pump, and connections for pressurization. This setup allowed to conduct the hydrogenation of CO₂ enabling the removal of the product phase from the bottom valve, refilling of the substrate solution under pressure as well as re-pressurization, while the autoclave was maintained at reaction temperature (Figure 6).

A MIBC-solution of catalyst 1 (25 mL) was combined with an equal amount of an aqueous solution of MEA at an amine loading of 20 weight-%. The MEA solution was saturated with small amount of MIBC to compensate for eventual crosssolubility from the catalyst solvent during recycling. The initial loading of complex 1 was adjusted to 5×10^{-3} mol% relative to the amount of amine. In the first loading at room temperature, the complex was not fully soluble in MIBC, but fully homogeneous yellow solutions were obtained for the organic phase at reaction temperature. The reaction mixture was saturated with CO₂ by vigorous stirring under 30 bar pressure, after which the CO₂ pressure was released to only 5 bar. This mixture was then pressurized with H₂ to reach a total of 90 bar. After constant pressure was reached, the phases were allowed to separate and the aqueous phase removed through the valve at the bottom, leaving the organic layer with small residues of the water phase in the reactor. This was then charged again with the aqueous MEA-solution as described above and the procedure repeated.



Figure 7. HCOOH/MEA ratio (bars) in the isolated aqueous phases and average TOF_{av} of the individual runs in the semi-continuous direct hydrogenation of CO₂-saturated aqueous MEA-solutions (details in SI and table S7).

The results of this procedure are summarized in Figure 6 showing the HCOOH/amine ratio in the isolated aqueous phases together with the TOF_{av} as judged from the time required for constant pressure. Until run 7, the reactions reached constant pressure within 50 to 90 min (see Table S7). From the amount of formate in the water phase, average TOF values can be estimated to be in the range of $10-14 \times 10^5 h^{-1}$ as lower limit for the catalyst activity under these conditions. The final HCOOH/MEA ratios in the aqueous phase varied between 0.6 and 0.8. From the eight run onwards, the time to reach constant pressure increased significantly. In the 11th cycle the reaction required 24 h to reach a constant pressure value, but still formed enough formic acid to result in a HCOOH/MEA ratio of 0.6. In total, the overall yield of formic acid relative to the amount of amine reached 70% in the aqueous phase, corresponding to a TTON of ~150.000. Even though the catalyst stability clearly requires further improvement for optimizing the recycling procedure towards fully continuous operation, the performance corresponds to the formation of 7.3 kg formic acid per gram of catalyst already at this early development stage of the system.

Summary and Outlook: This investigation demonstrates the efficacy of biphasic catalysis for the hydrogenation of CO₂ to produce aqueous formate solutions directly from amine solutions such as used in carbon capture technologies. A highly active and easily accessible Ru-catalyst was immobilized either in a hydrophobic ionic liquid or in an organic solvent while water was used as the product phase. Whereas the amines partition between the two phases according to their polarities, the formate-amine-adducts reside almost quantitatively in the water phase in all cases studied here. The cheap solvent methylisobutylcarbinol (MIBC) provided the best combination of high catalyst activity and stability with simple product separation. Initial turnover frequencies in the range of $10^4 - 10^5$ h⁻¹ were achieved which could be retained to 63% over seven recycles using mono-ethanloamine (MEA) and almost completely over ten cycles using methyldiethanolamine (Aminosol CST 115[®]). Very low catalyst leaching values into the product phase (\leq 0.26% for Ru, \leq 1.00% for P in average per run) were found using both scrubbing amines.

A semi-continuous process was realized validating the conceptual viability of this approach. A total turnover number (TTON) of ca. 150 000 mol of HCOOH per mol of catalyst was achieved over 11 runs using CO₂-saturated aqueous solutions of MEA as substrate phase. Thus, feedstocks mimicking the aqueous stream from a CO₂ capture unit^[39] could be effectively and directly hydrogenated resulting in a unique example for an integrated carbon capture and utilization (CCU) process. Further research to elucidate the compatibility of this or other catalytic systems with potential impurities or catalyst poisons from real scrubbing solutions seem very promising on basis of these results.^[40]

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Keywords: CO₂ hydrogenation • formic acid • biphasic catalysis • ruthenium phosphine catalysts • carbon capture and utilization (CCU)

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- [32] This experiment series was repeated obtaining similar results (see Figure S8)
- [33] The very fast reaction does not allow to precisely define the position of the tangent for calculating the TOF_{ini} and the exact time of reaction completion for the determination of the TOF value and minor change for instance of the point of completion causes large deviation of TOF values (e.g. completion within 3 min: TOF ~35 000 h⁻¹; completion after 2.75 min: TOF ~45 000 h⁻¹)
- [34] After the second run, the determination of the yield of the single recycling experiments became increasingly inaccurate because of the unknown amount of left i) unconverted amine in the catalyst phase and ii) product containing water phase present after each run. Consequently, no TON, TOF and initial TOF were calculated for the

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

ESSAY

An integrated process for the synthesis of formate-amine-adducts based on aqueous biphasic catalysis is presented. The solvent pair $MIBC/H_2O$ led to the most productive system using a Ru-dppm complex and repetitive use of the catalyst phase was demonstrated. Noteworthy, this approach enabled the direct hydrogenation of aqueous solutions of monoethanolamine methyland diethanolamine such as used in carbon capture technologies achieving a TTON of up to 150.000.

Layout 2:

ESSAY



Martin Scott, Beatriz Blas Molinos, Christian Westhues, Giancarlo Franciò* and Walter Leitner*

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Title

((Insert TOC Graphic here))

Aqueous Biphasic Systems for the Synthesis of Formates via Catalytic CO₂-Hydrogenation: Integrated Reaction and Product Separation for CO₂-scrubbing solutions