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

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Introduction

Increased interest in closed carbon cycles across different industrial sectors has resulted in renewed strong impulses toward investigations of the use of carbon dioxide as a chemical feedstock. The physico-chemical properties and non-toxicity of CO₂ together with its abundant availability at highly concentrated point sources endorse its potential application as C1 building block. In particular, the hydrogenation of carbon dioxide into formic acid and formate adducts has been widely studied because of their broad industrial use as biomass preservatives, in the textile industry, as additive for pharmaceuticals and food, and in possible future opportunities as hydrogen storage materials or as safe CO and phosgene substitutes. In recent decades, very potent homogeneous Ru-, Ir-, Fe-, or Co-based catalytic systems have been developed for this transformation. However, the next crucial steps toward the applications of such systems—namely their integration into CO₂-based value chains with separation and recycling of the homogeneous catalyst—have to date rarely been addressed.

Owing to the interplay of thermodynamic and kinetic boundary conditions for the transformation of CO₂ and H₂ into formic acid, the catalyst system comprising the molecular active species and the reaction medium has to be carefully selected. In this context, aqueous biphasic systems seem particularly attractive as aqueous amine solutions are used on commercial scale as CO₂-scrubbing media. At the same time, they offer the potential to separate or immobilize the organometallic active species if combined with hydrophobic solvents as the catalyst phase. To our knowledge, however, the application of industrially used scrubbing amines in biphasic aqueous systems with in situ catalyst removal has not been demonstrated.
As early as 1989, BP chemicals described in a patent a biphasic system comprising aliphatic or aromatic hydrocarbons as the catalyst phase and alcohols or water as the product phase for HCOOH adducts with trialkylamines such as NEt₃. Although the catalyst solution was re-used three times, very low turnover numbers (TONs) 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 ionic liquids (ILs) as the catalyst phase. A maximum turnover frequency (TOF) of 450 h⁻¹ was obtained, 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. The catalyst was largely retained in the excess amine and separated from the polar product phase by back-extraction 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 by using a water-soluble Wilkinson-type catalyst. This approach was successfully extended to solutions comprising the ethanamines used as bases in commercial scale CO₂-scrubbing processes. Although a variety of catalysts have been described since then for CO₂ hydrogenation in aqueous solutions using amines or inorganic bases and even under base-free conditions, this early work appears to remain the only study employing commercially relevant scrubbing amines. While the present manuscript was in preparation, a paper by Olah, Prakash and co-workers also reported 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.

We present herein 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. Different ILs and organic solvents have been evaluated with a focus on productivity and integrated catalyst separation for a variety of amines including methyl diethanolamine (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 ruthenium complex 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 monoethanolamine solutions of CO₂ as a feedstock, demonstrating potential integration with carbon capture technologies.

**Results and Discussion**

The complex cis-[Ru(dppm)₂Cl₂] (dppm = bis-diphenylphosphinomethane) was used as catalyst precursor throughout the present study. It was synthesized by adapting literature known procedures 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. Complex 1 also shows solubility in a broad range of solvents from high to moderate polarity, making it particularly attractive for the envisaged biphasic systems.

As a first approach, the combination of hydrophilic ionic liquids (ILs) and water was investigated. Preliminary CO₂ 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] (EMIM = 1-ethyl-3-methylimidazolium) was used as the catalyst phase. In contrast, the more hydrophobic IL [OMIM][NTf₂] (OMIM = 1-octyl-3-methylimidazolium) with a long alky 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.

Partitioning experiments were carried out to evaluate the solubility behavior of the amines and their corresponding for-
mate adducts in the biphasic medium (Table 1). As expected, the amines partition more readily in the aqueous phase, in accordance with 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 RT) 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 dimethylformamide. The reaction progress was followed by monitoring the pressure drop from which an initial turnover frequency (TOF₉₅) was calculated (see the Supporting Information, Figures S1 and S4). At the end of the reaction, a mixture of acetone and DMSO (1:1 v/v) was added to the biphasic system, thereby affording a single phase, which was analyzed by ¹H NMR spectroscopy with cyclohexene or mesitylene as internal standard and a pulse delay of 20 s. The accuracy of this method was calibrated by using HCOOH/amine standard solutions and deviations of ±5% were found. No signals indicating amide formation were detected and maximum HCOOH/amine ratios up to 1:1 were observed, in accordance with the limiting conversion already shown in previous studies using single-phase aqueous media.[16, 17] In comparison, water-free systems showed higher HCOOH/amine ratios up to 1.6:1.[10c]

High CO₂ conversions into 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 TOFₙ₅ of about 5000 h⁻¹ was achieved, which was independently of the catalyst loading used (Table 2, entries 1 and 2). This indicates that no mass transfer limitations were in effect 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 HNIPr₂ and NET₃ (Table 2, entries 3–6). Higher values of TOFₙ₅ were obtained with both amines at higher catalyst loading, possibly indicating some catalyst deactivation at lower catalyst concentrations.

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 RT 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. A thin aqueous layer (ca. 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 CO₂/H₂ and heated to 70 °C.[21] The pressure–time curves of four consecutive experiments are shown in Figure 2.

This procedure allowed for effective recycling of the IL phase, but the reaction rate after each run decreased significantly, indicating some catalyst deactivation. A total TON (TON) 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 used amine amount (see the Supporting Information, 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 inductively coupled plasma mass spectrometry (ICP–MS). Whereas the Ru leaching was very low, ranging from 0.3 to 0.8% per run, the P leaching was more pronounced with values ranging from 1.2 to 2.3% per run, with total losses 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 the Supporting Information, Table S3).

Table 1. Partitioning [%] of different amines and the corresponding formate adducts in H₂O/OMIM[N(Tf₂)].[a]

| Amine     | Free amine in H₂O phase | Free amine in IL phase | Formate–amine adduct in H₂O phase |
|-----------|-------------------------|------------------------|----------------------------------|
| HNMe₂     | 56                      | 44                     | >95                              |
| HNIPr₂    | 23                      | 77                     | >95                              |
| NET₃      | 7                       | 93                     | >95                              |

[a] Determined by ¹H NMR spectroscopy (accuracy ±5%), see the Supporting Information for details.

Table 2. Ru-catalyzed hydrogenation of CO₂ in the presence of different amines in the biphasic system [OMIM][N(Tf₂)]/H₂O.[b]

| Entry | Amine     | Cat. (mol/mol)[c] | t [min] | HCOOH/amine (mol/mol) | TON | TOFₙ₅ (h⁻¹) |
|-------|-----------|------------------|--------|-----------------------|-----|-------------|
| 1     | HNMe₂     | 0.05             | 53     | n.d.                  | 1875| 5340        |
| 2     | HNMe₂     | 0.13             | 20     | n.d.                  | 690| 5060        |
| 3     | HNIPr₂    | 0.05             | 316    | 96/100                | 1720| 300         |
| 4     | HNIPr₂    | 0.13             | 63     | 91/100                | 690| 1080        |
| 5     | NET₃      | 0.05             | 212    | 95/100                | 1615| 740         |
| 6     | NET₃      | 0.13             | 50     | 92/100                | 690| 2040        |

[a] Reaction conditions: 10 mL window autoclave, amine (ca. 7.9 mmol), IL (ca. 1 mL), H₂O (1.5–1.7 mL), total pressure = 90 bar (60 bar H₂, 30 bar CO₂), pressurized at RT, 70 °C, vigorous stirring. [b] Based on amine loading. [c] Calculated from pressure–time profiles (see the Supporting Information 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.
Since the IL-based biphasic system demonstrated in principle the feasibility of the approach but showed limited stability, we turned our interest to organic/H$_2$O systems. Various water-immiscible solvents with quite different physicochemical properties were evaluated. Toluene, already used in the BP system,\textsuperscript{[14b,c]} was included as a representative low-polarity solvent, whereas biobased 2-methyltetrahydrofuran (2-MTHF)\textsuperscript{[26]} and cyclopentyl methyl ether (CPME)\textsuperscript{[27]} were selected as water-immiscible ethers with moderate polarities. The cheap and readily available alcohol methyl isobutyl carbinol (MIBC) was chosen as a protic yet water-immiscible polar solvent.\textsuperscript{[28]} These solvents are all regarded as industrially acceptable according to the solvent selection guidelines.\textsuperscript{[29]} Dimethyamine, triethylamine, and monoethanolamine (MEA), as a prototypical example of a scrubbing amine applied on commercial scale,\textsuperscript{[30]} were used as the amine components.

The partitioning of the amines in the different organic/H$_2$O systems reflects again the amine polarity and increasing preference for the aqueous phase was observed for NEt$_3$ < MEA < HNMe$_2$ in all cases. The absolute values obviously correlate with the polarity of the individual organic solvents (see the Supporting Information, Table S1). Again, the corresponding formate adducts partitioned exclusively in the aqueous phase, warranting the prerequisite for efficient biphasic catalysis and separation.

The hydrogenation reactions were performed under the same conditions as before, with a catalyst loading of 0.05 mol% relative to the amine. The benchmark NEt$_3$ was used as amine and at least three recycling experiments were conducted for evaluating the different organic/H$_2$O systems (Table 3).\textsuperscript{[31]}

Toluene resulted in the lowest reaction rate of all solvents with only small variations over the three runs (see the Supporting Information, 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/H$_2$O system. An almost ten times faster reaction than in toluene was observed when using CPME as the catalyst phase (Table 3, entry 2) although 1 was again not completely soluble in this medium. A significant decrease in 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 the Supporting Information, 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 CO$_2$ hydrogenation was achieved (see the Supporting Information, Figures S7 and S8 for pressure–time profiles). In the first and second runs, the catalyst showed a TOF$_{ini}$ of approximately 11 000 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.\textsuperscript{[32]}

Finally, an excellent combination of high activity and endurance was obtained when MIBC was used as catalyst phase (Table 3, entries 4–7). In the first run the catalyst showed only

![Figure 2. Pressure-time curves for the CO$_2$ hydrogenation in the biphasic system [OMIM][NTf$_2$]/H$_2$O with HNMe$_2$ as base. Conditions: 20 mL window autoclave, HNMe$_2$ (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), H$_2$O (3 mL), 90 bar total pressure (60 bar H$_2$, 30 bar CO$_2$, pressurized at RT, 70 °C, vigorous stirring.)](Image)

Table 3. Hydrogenation of CO$_2$ with the different amines in the system organic/H$_2$O.$^*$

| Entry | Solvent | Amine   | Runs | t [min]$^a$ | Yield [%]$^a$ | HCOOH/amine [mol/mol]$^a$ | TTON | TOF$_{ini}$ [h$^{-1}$]$^a$ | TOF$_{max}$ [h$^{-1}$]$^a$ |
|-------|---------|---------|------|------------|-------------|------------------------|------|------------------------|------------------------|
| 1     | toluene | NEt$_3$ | 3    | 415$^f$   | 69          | 90/100                 | 4010 | 262                    | 420$^f$                |
| 2     | CPME    | NEt$_3$ | 3    | 19$^f$    | 68          | 89/100                 | 3930 | 3412                   | 471$^{f,g}$            |
| 3     | 2-MTHF  | NEt$_3$ | 3    | 14$^f$    | 49          | 66/100                 | 2980 | 7300                   | 11 200$^f$             |
| 4     | MIBC    | NEt$_3$ | 10   | 3$^f$     | 75          | 86/100                 | 14 540 | $\geq$ 35 000         | 180 000$^f$            |
| 5     | MIBC    | HNMe$_2$| 7    | 7$^f$     | 85          | 93/100                 | 11 430 | 16 500                 | 31 400$^{f,g}$         |
| 6     | MIBC    | MEA     | 7    | 10$^f$    | 83          | 92/100                 | 11 340 | 15 200                 | 17 300$^f$             |
| 7     | MIBC    | Aminosol CST 115$^h$ | 10 | 12$^f$ | 83 | 100/100 | 18 170 | 8109 | 41 000$^{f,g}$ |

$^a$ 10 mL window autoclave, amine (ca. 7.9 mmol), 1 (4.1 mmol) organic solvent (1.5 mL), H$_2$O (2 mL), total pressure 90 bar (60 bar H$_2$, 30 bar CO$_2$, pressurised at RT), 70 °C, for more time details, see the Supporting Information, 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 $^d$ H NMR spectroscopy. $^e$ Average HCOOH/ICP–MS ratio of all runs. $^f$ Calculated from pressure–time profiles (see the Supporting Information for complete data). $^g$ Determined for the second run. $^h$ Determined for the first run. $^i$ 1:1 v/v mixture with water, 9.0 mmol per run (for detailed procedure, see the Supporting Information). $^j$ Average over all runs.
moderate activity. After this induction period, however, the system exhibited excellent performance in the second run and the reaction was completed within about 3 minutes with a TOF$_{\text{ini}}$ of approximately 180,000 h$^{-1}$ and a TOF$_{\text{av}}$ of approximately 35,000 h$^{-1}$ (Figure 3 and Figures S4 and S9 in the Supporting Information).

The activity remained high in the third run and the repetition of 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.$^{[34]}$ 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 roughly 14,500 could be achieved over the 10 runs in the system NEt$_3$/MIBC/H$_2$O (Table 3, entry 4).

The use of HNMe$_2$ also led to fast hydrogenation of CO$_2$ in the biphasic MIBC/H$_2$O system. However, loss of catalyst activity was more pronounced with this amine (see the Supporting Information, Figures S11 and S12). The initial gas consumption rate in the 7th run dropped to 12% as compared to the 1st run. A TTON of approximately 11,400 was obtained over seven runs (Table 3, entry 5, and Figures S10 to S12 in the Supporting Information).

Gratifyingly, the MIBC/H$_2$O system proved particularly effective in combination with MEA as amine component (Table 3, entry 6). Under standard conditions, excellent activity corresponding to a TOF$_{\text{ini}}$ of 17,300 h$^{-1}$ was already observed 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 inferred from the pressure–time profiles (Figure 4 and Figures S13 and S14 in the Supporting Information), and 63% of the initial activity was still observed after 7 runs. A TTON of 11,300 was achieved at this stage.

Even more stable catalyst performances were observed with the industrially used scrubbing amine solution Aminosol CST 115$^{[35]}$ in a 1:1 v/v mixture with water (Table 3, entry 7). In contrast to 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 did not allow a defined start of the reaction, the stirrer was switched on from the beginning of the heating period, taking roughly 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$_{\text{ini}}$ of 41,000 h$^{-1}$ was observed already in the first run. 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 18,170 was achieved in 10 runs (Table S5).

Determination of Ru and P leaching through ICP–MS measurements of the content in the aqueous phase confirmed the efficacy of the biphasic system MIBC/H$_2$O (Table 4). Ru leaching
ranging from 1.2–2.9% in each run was found in the recycling experiments carried out in the presence of NET$_3$ or HNMe$_2$, accounting for total Ru losses of 9.5% and 10.6%, respectively, after 5 runs (Table 4). Lower P leaching was found in the case of NET$_3$ (4.8% total P loss after 5 runs) compared to HNMe$_2$ (10.9% total P loss after 5 runs). Notably, significantly better catalyst retention was achieved in the presence of MEA, with leaching values considerably below 1% per each run. Total P and Ru leaching below 2% of the original catalyst loading, even after 5 runs, was determined by ICP–MS, corroborating the high potential of the MEA/MIBC/H$_2$O system, which combines readily available components, high catalyst stability, and low leaching. Very low Ru leaching of 0.21% per run, averaged over ten cycles, was also found in the presence of Aminosol CST 115, whereas P leaching was significantly higher, with an average value of 1% per run (see the Supporting Information, 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 plays a major role for the performance in the recycling sequence.

These very positive results prompted 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. To this end, the use of an aqueous solution of MEA at a loading of around 20 wt% which was pre-saturated with CO$_2$ at low overpressures, was examined as feedstock for direct hydrogenation (Table 5).

A MEA solution with just 2 bar CO$_2$ overpressure could be hydrogenated in 59% yield using 88 bar H$_2$ (Table 5, entry 1). The same yield was achieved by using a slightly higher CO$_2$ overpressure of 5 bar and a much lower H$_2$ pressure ($p_{H_2}$) of 25 bar (Table 5, entry 2). Increasing the hydrogen pressure to 55 bar led to 74% yield (Table 5, entry 3). A similar result could also be obtained at an identical total pressure of 90 bar, increasing the partial pressure of CO$_2$ ($p_{CO_2}$) and reducing $p_{H_2}$ to 75 bar (Table 5 entry 5). These experiments show that saturated MEA-solutions with low CO$_2$ overpressure can serve directly as feedstock for the hydrogenation of carbon dioxide to yield nearly stoichiometric amounts of formic acid in relation to amine.

Finally, the system MEA/MIBC/H$_2$O was selected for validating this approach under semicontinuous operation. 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 CO$_2$ 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).

### Table 4. Leaching values [%] for the first 5 runs in the MIBC/H$_2$O system [see Figure 3 for NET$_3$, Figure S11 (see the Supporting Information) for HNMe$_2$, and Figure 4 for MEA].

| Run | NEt$_3$ Ru | NEt$_3$ P | HNMe$_2$ Ru | HNMe$_2$ P |
|-----|------------|-----------|-------------|-----------|
| 1   | 1.30       | 0.01      | 1.96        | 0.01      |
| 2   | 1.22       | 0.02      | 1.22        | 0.02      |
| 3   | 2.09       | 0.03      | 2.09        | 0.03      |
| 4   | 2.90       | 0.04      | 2.83        | 0.04      |
| 5   | 2.02       | 0.05      | 2.46        | 0.05      |

[a] determined by ICP–MS measurement of the concentration in the aqueous product phase and expressed as a percentage of the initial catalyst loading.

### Table 5. Hydrogenation of CO$_2$ with MEA in MIBC/H$_2$O.

| Entry | $p_{CO_2}$ [bar] | $p_{H_2}$ [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 (ca. 7.9 mmol). 1 (4.1 mmol), MIBC (1.5 mL), H$_2$O (2 mL); 70 °C, t = 10–15 min (time to constant pressure in the reactor), vigorous stirring. [b] Yield refers to the initial amount of amine and calculated from the formate concentration in the isolated aqueous product phase as quantified by $^1$H NMR spectroscopy.

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 wt%. The MEA solution was saturated with a small amount of MIBC to compensate for minor cross-solubility from the catalyst solvent during recycling. The loading of complex 1 was adjusted to $5 \times 10^{-3}$ mol% relative to the initial amount of amine. Although the complex was initially not completely dissolved at RT in MIBC, fully homogeneous yellow solutions of the organic phase were obtained at reaction temperature. The reaction mixture was saturated with CO$_2$ by vigorous stirring under 30 bar pressure, after which the CO$_2$ pres-
ure 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 by using the HPLC pump with a new batch of aqueous MEA-solution as described above and the procedure repeated.

The results of this procedure are summarized in Figure 7, which shows the HCOOH/amine ratio in the isolated aqueous phases together with the TOFₚₑ as derived from the time required to attain constant pressure. Until run 7, the reactions reached constant pressure within 50 to 90 min (see the Supporting Information, 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 to 10⁻¹⁰ h⁻¹ as a 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 eighth run onwards, the time to reach constant pressure increased significantly. In the 11th cycle, the reaction required 24 h to reach constant pressure, 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 roughly 150 000. Even though the catalyst stability clearly requires further improvement for optimizing the recycling procedure towards fully continuous operation, the performance already corresponds to the formation of 7.3 kg formic acid per gram of catalyst at this early stage in the system’s development.

![Figure 7. HCOOH/MEA ratio (bars) in the isolated aqueous phases and average TOFₚₑ of the individual runs in the semi-continuous direct hydrogenation of CO₂-saturated aqueous MEA-solutions](image)

**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 residues almost quantitatively in the water phase in all cases studied here. The cheap solvent methyl isobutyl carbinox (MIBC) provided the best combination of high catalyst activity and stability with simple product separation. Initial turnover frequencies in the range of 10⁴ h⁻¹ were achieved, which could be retained to 63% of the initial value over seven recycles when using monoethanolamine (MEA) and almost completely over ten cycles when using methyl diethanolamine (Aminosol CST 115).

Very low levels of catalyst leaching into the product phase (<0.26% per run for Ru, ≤1% per run for P on average) were found when using both scrubbing amines.

A semicontinuous process was realized, validating the conceptual viability of this approach. A total turnover number (TON) of approximately 150 000 mol of HCOOH per mol of catalyst was achieved over 11 runs by using CO₂-saturated aqueous solutions of MEA as the 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 of an integrated carbon capture and utilization (CCU) process. Further research to establish the compatibility of this or other catalytic systems with potential impurities or catalyst poisons from real scrubbing solutions holds much promise on basis of these results.[40]

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** biphasic catalysis • carbon capture • CO₂ hydrogenation • formic acid • ruthenium

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This experiment series was repeated, affording similar results (see the Supporting Information, Figure 58).

The very fast reaction does not allow precise definition of the position of the tangent for calculating the TOFav, and the exact time of reaction completion for the determination of the TOFmax value. Minor changes, for instance in the point of completion, cause large deviation of TOFmax values (e.g., completion within 3 min: TOFav = 35 000 h−1; completion after 2.75 min: TOFmax = 45 000 h−1).

After the second run, the determination of the yield of the single recycling experiments became increasingly inaccurate because of the unknown amount of left 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 individual recycling experiments after the second run (see the Supporting Information for complete data).

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