Electronic Supplementary Material (ESI) for Green Chemistry.


Supporting information

# $CO_2$ hydrogenation to formic acid in biphasic systems using aqueous solutions of amino acids as product phase

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## List of contents

# Material and Methods

## General

All reagents and solvents were purchased by commercial suppliers. Procedures using air sensitive compounds were carried out under an inert argon atmosphere (argon 4.8). For synthesis, the chemicals were degassed, and solvents were additionally dried over 3 Å molecular sieves before use.

For catalytic reactions, the solvents were degassed via a glass frit by bubbling with Argon for 30 minutes before use. Reaction gases hydrogen 5.0 and carbon dioxide 4.6 were used without further purification.

## NMR analytic

$^{1}H$, $^{13}C$ and $^{31}P$ NMR measurements were conducted at room temperature on a Bruker AS 400 (Bruker Corporation, Billerica, MA, USA) spectrometer. The chemical shift δ is given in ppm, the coupling constant J in Hertz. The multiplicities are denoted as s (singlet), d (doublet), t (triplet) and m (multiplet). The chemical shift was referenced to the solvent residual signal. Quantitative analysis was conducted using maleic acid as internal standard for aqueous solutions and mesitylene for organic solutions.

## ICP-MS analytic

ICP-MS was measured on an ICP-MS triple quadrupole (Agilent, model 8800) in an aqueous matrix.

## Calculation of Initial Turnover Frequency ($TOF_{ini}$) from the pressure drop

The pressure-time curves for the experiments carried out in 10 mL window autoclaves were recorded using a digital pressure gauge connected to a PC. The data were acquired through the LabView$^{tm}$ software (National Instruments). The software Origin Pro 9.6 was used for visualization and analysis of the data. The obtained pressure time curves were smoothed using the implemented Savitzky-Golay filter (example see Figure S1). For better comparability, the pressure was converted into the Δp by subtracting the measured pressure before the start of the reaction and setting this time as t = 0 h (see Figure S2).

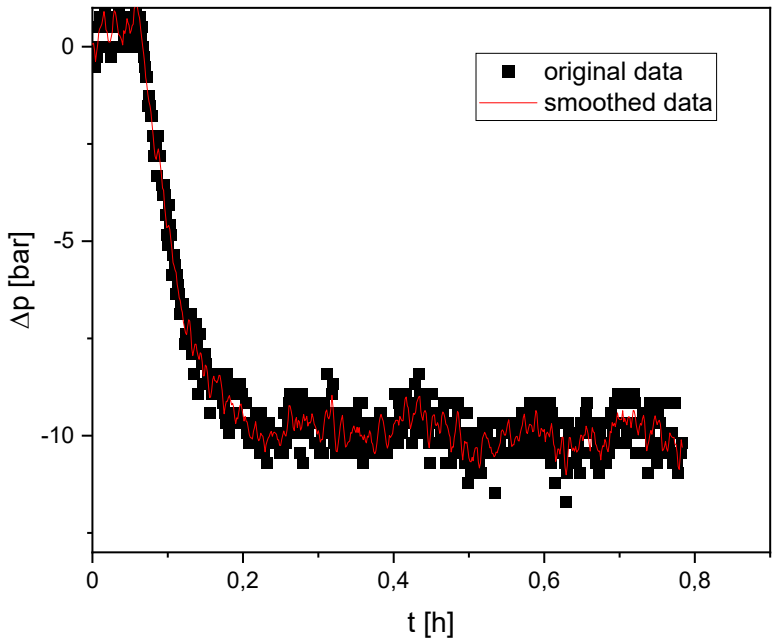



*Figure S1: Exemplary pressure-time curve with original and smoothed date, respective experiment see ESI Tab. S1, entry 1.*

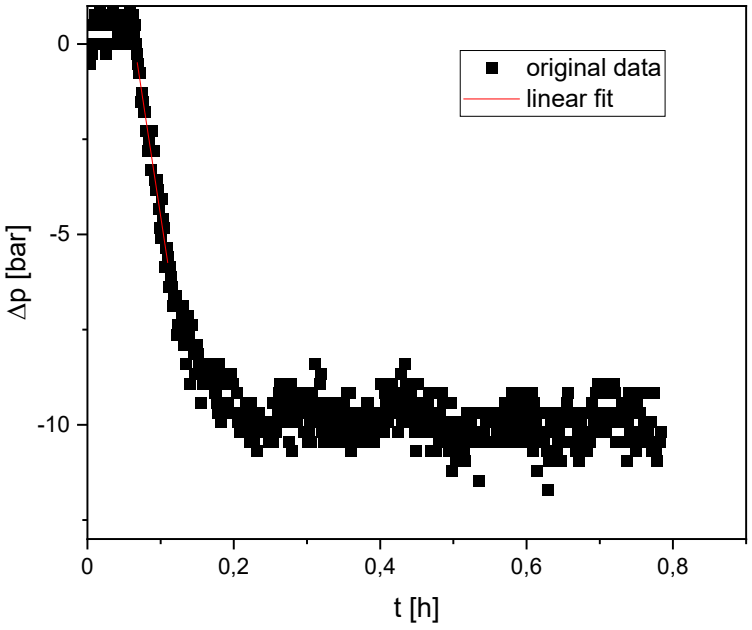



*Figure S2: Pressure-time curve converted to Δp and reaction start at t = 0 h with linear fit for determination of $TOF_{ini}$, respective experiment ESI Tab. S1, entry 1.*

As shown in the following exemplary equations (Tab. S1, entry 1), the slope of the initial pressure drop (92.5 bar $h^{-1}$), the catalyst loading (1.04 µmol), the amount of FA (2.376 mmol, determined via $^1$H NMR) and the pressure drop Δp = 8.9 bar were used to calculate the initial turnover frequency $TOF_{ini}$ (eq 1-3):

$$m_{\Delta p} = 92.5\ bar\ h^{-1}, \Delta p = 8.9\ bar, Y = 2.376\ mmol, n_{cat} = 1.00\ \mu mol$$

$$\frac{Y}{\Delta p} = \frac{2.376\ mmol}{8.9\ bar} = 0.267\ mmol\ bar^{-1} \quad (1)$$

$$m_n = m_{\Delta p} \cdot \frac{Y}{\Delta p} = 92.5\ bar\ h^{-1} \cdot 0.267\ mmol\ bar^{-1} = 24.69\ mmol\ h^{-1} \quad (2)$$

$$TOF_{ini} = \frac{m_n}{n_{cat}} = \frac{24.69\ mmol\ min^{-1}}{1.04\ \mu mol} = 23\ 744\ h^{-1} \quad (3)$$

**Quantification from $H_2$-flow data**

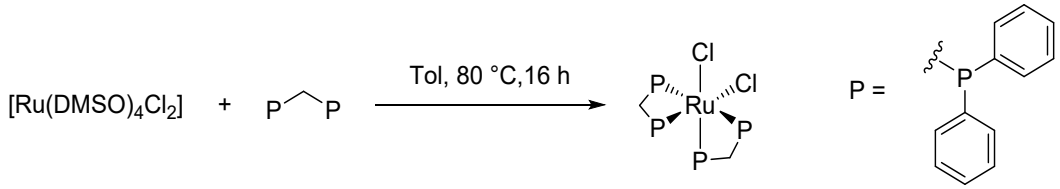
The $H_2$ mass-flow was integrated with the software Origin from OriginLab. This results in the total amount of $H_2$ consumed in mL, which was converted into mmol considering the density of $H_2$ under reaction conditions.

$$n_{H2} = \frac{V_{H2} \cdot \rho_{H2}}{M_{H2}} = \frac{2044.88\ mL_N \cdot 8.3775 \cdot 10^{-5}\ g\ mL^{-1}}{2.10588\ g\ mol^{-1}} = 84.962\ mmol \quad (4)$$

The curve resulting from the time resolved integration was fitted linearly from 60-120 min for determination of the initial TOF.

# Syntheses

### Synthesis of *cis*-[$RuCl_2(dppm)_2$] (Ru-dppm)

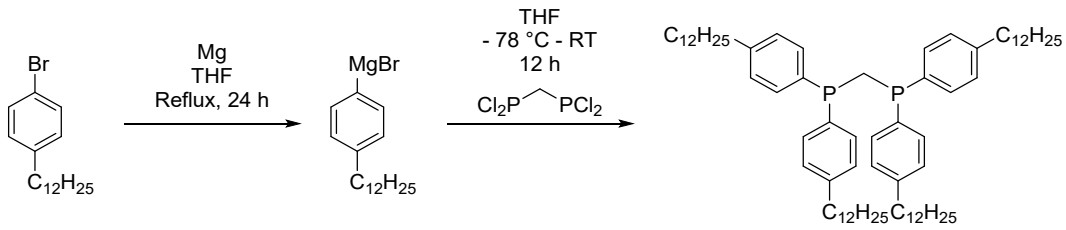



The synthesis was performed according to a literature procedure.[1] In a *Schlenk*-tube a suspension of [$Ru(DMSO)_4Cl_2$] (0.41 g, 0.84 mmol, 1 eq.) and bis-bis(diphenylphosphanyl)methane (dppm) (0.67 g, 1.68 mmol, 2 eq.) in toluene (30 mL) was stirred at 80 °C for 16 h. The colour changed from dark yellow/gold to a lighter, citrus-like yellow. The progress of the reaction was checked with $^{31}$P-NMR measurements in $CD_2Cl_2$. After completion, the solvent was removed *via* cannula, the residue was washed three times with pentane (10 mL) and two times with $Et_2O$ (10 mL). The resulting yellow solid was then dried *in vacuo* (0.703 mg, 0.748 mmol, 89 % yield).

**$^1$H{$^{31}$P}-NMR:** **($CD_2Cl_2$, 400,1 MHz)**: δ = 8,20 (d, $^3J_{H,H}$ = 7,4 Hz, 4H, Ar-H), 7,87 (d, $^3J_{H,H}$ = 7,4 Hz, 4H, H-Ar), 7,49-7,00 (m, 20H, Ar-H), 6,89 (d, $^3J_{H,H}$ = 7,7 Hz, 4H, Ar-H), 6,80 (t, $^3J_{H,H}$ = 7,7 Hz, 4H, Ar-H), 6,64 (d, $^3J_{H,H}$ = 7,6 Hz, 4H, Ar-H), 5,01 (d, $^2J_{H,H}$ = 15,3 Hz, 2H, CH), 4,72 (d, $^2J_{H,H}$ = 15,3 Hz, 2H, CH) ppm.

**$^{31}$P{$^1$H}-NMR:** **($CD_2Cl_2$, 242.1 MHz):** δ = 0,0 (t, $J_{P,P}$ = 35,9 Hz, 2P, PPh), −26,0 (t, $J_{P,P}$ = 35,9 Hz, 2P, PPh) ppm.

### Synthesis of bis(bis(4-dodecylphenyl)phosphanyl)methane ($C_{12}$-dppm)



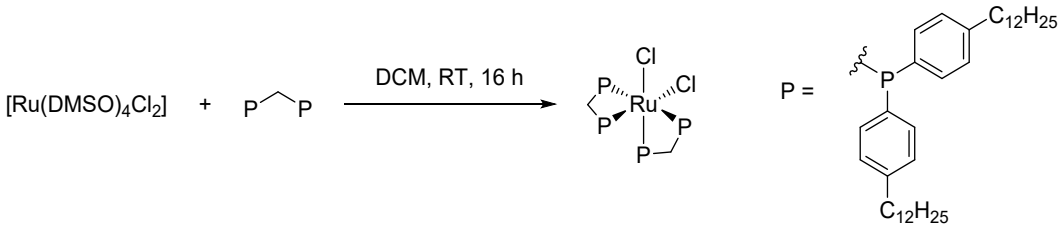

The synthesis was performed according to a literature procedure.[2] In a *Schlenk*-flask THF (15 mL) and magnesium turnings (0.370 g, 15.2 mmol, 6.6 eq.) were added and heated to 40 °C. A solution of 1-bromo-4-dodecylbenzene (4.030 g, 12.4 mmol, 5.4 eq.) in THF (10 mL) was added dropwise in a manner that the solution was refluxing self-sustainingly. After complete addition, the solution was refluxed for additional 12 h. The resulting Grignard-

solution was filtered and separated from residual magnesium. This solution was cooled to -78 °C and a solution of 1,2-bis(dichlorophosphino)methane (0.500 g, 2.3 mmol, 1.0 eq.) in THF (4.5 mL) was added over 45 minutes. The mixture was then allowed to warm to room temperature and stirred for 12 h. Completion of the reaction was confirmed via 31P-NMR. An aqueous, degassed $NH_4Cl$-solution (20 mL) was then added, the organic phase separated and the aqueous phase extracted with n-pentane (3 × 10 mL). The combined organic phases were dried over $Na_2SO_4$ and filtered over Celite®. The solvent was removed in vacuo and excess dodecylbenzene was removed at high vacuum (1 × $10^{-3}$ mbar) and 120 °C resulting in a colourless, viscous oil (2.07 g, 1.96 mmol, 85 % yield).

**$^1H\{^{31}P\}$-NMR:** **($CDCl_3$, 400,1 MHz)**: δ =7,33 (d, $^3J_{H,H}$ = 7,83 Hz, 8H, Ar-*H*), 7,12 (d, $^3J_{H,H}$ = 7,83 Hz, 8H, *H*-Ar), 2,77z (s, 2H, P-C*H*$_2$-P), 2,57 (t, $^3J_{H,H}$ = 7,66 Hz, 8H, Ar-C*H*$_2$-CH$_2$-) 1,59 (m, 6H, Ar-CH$_2$-C*H*$_2$) 1,30 (m, 40H, -CH$_2$-(C*H*$_2$)$_5$-CH$_3$), 0,88 (t, $^3J_{H,H}$ = 6,57 Hz, 12H, -CH$_2$-(CH$_2$)$_5$- C*H*$_3$) ppm.

**$^{31}P\{^1H\}$-NMR:** **($CDCl_3$, 242.1 MHz):** δ = −25.0 (s, 2P, *P*Ph) ppm.

**Synthesis of *cis*-[$RuCl_2$($C_{12}$-dppm)$_2$] (Ru-$C_{12}$-dppm)**




The synthesis was performed according to a literature procedure.[2] In a *Schlenk*-tube a suspension of [$Ru(DMSO)_4Cl_2$] (0.41 g, 0.84 mmol, 1 eq.) and $C_{12}$-dppm (1.78 g, 1.68 mmol, 2 eq.) in $CH_2Cl_2$ (20 mL) was stirred at room temperature for 16 h. During this time, the yellow suspension became a clear solution changing the colour from colourless over pale yellow to orange. The progress of the reaction was monitored with $^{31}$P-NMR. After completion, the solvent was removed *in vacuo*, the residue dissolved in *n*-decane (15 mL) and washed with methanol (3 × 10 mL) to remove DMSO. The emulsion of methanol and *n*-decane was separated *via* centrifugation. After removal of *n*-decane *in vacuo*, a resinous, orange solid was obtained (1.73 g, 0.756 mmol, 90 % yield).

**$^{1}H\{^{31}P\}$-NMR:** **($CDCl_3$, 400,1 MHz):** δ = 8,07 (d, $^{3}J_{H,H}$ = 8,03 Hz, 4H, Ar-H), 7,80 (d, $^{3}J_{H,H}$ = 8,03 Hz, 4H, Ar-H), 7,15 (d, $^{3}J_{H,H}$ = 8,03 Hz, 4H, Ar-H), 6,88 (d, $^{3}J_{H,H}$ = 8,03 Hz, 4H, Ar-H), 6,75 (d, $^{3}J_{H,H}$ = 8,20 Hz, 4H, Ar-H), 6,72 (d, $^{3}J_{H,H}$ = 8,20 Hz, 4H, Ar-H), 6,45 (d, $^{3}J_{H,H}$ = 8,05 Hz, 4H, Ar-H), 6,25 (d, $^{3}J_{H,H}$ = 8,05 Hz, 4H, Ar-H), 4,68 (d, $^{2}J_{H,H}$ = 15,27 Hz, 2H,P-$CH_2$-P), 4,39 (d, $^{2}J_{H,H}$ = 15,27 Hz, 2H,P-$CH_2$-P), 2,56-2,28 (m, 8H, Ar-$CH_2$-$CH_2$), 1,59-1,37 (m, 8H, Ar-$CH_2$-$CH_2$), 1,29-1,05 (m, 144H, -$CH_2$-), 0,84-0,75 (m, 24H, -$CH_3$) ppm.

**$^{31}P\{^{1}H\}$-NMR:** **($CDCl_3$, 242,1 MHz):** δ = −1,7 (t, 2P, $^{3}J_{P,P}$ = 37,2 Hz *P*Ph), −28,9 (t, 2P, $^{3}J_{P,P}$ = 37,2 Hz *P*Ph) ppm.

# Catalytic experiments

### General procedure for $CO_2$ hydrogenation in single batch experiments

High pressure reactions were carried out in 10 mL stainless steel window autoclaves built and maintained by the mechanical workshop of the *Institut für Technische und Makromolekulare Chemie* of RWTH Aachen University. The autoclaves were equipped with a magnetic stir bar and a digital pressure gauge. To exclude oxygen from the system, vacuum was applied ($< 1 \times 10^{-2}$ mbar) in preparation for the experiments followed by flushing with argon. This procedure was repeated at least three times. The respective amounts of aqueous base-solution and catalyst solution were added in argon counterflow. The autoclave was sealed and pressurized with $CO_2$ (30 bar) and $H_2$ (60 bar) at r.t. (total pressure 90 bar). $CO_2$ pressurization took about 2-5 minutes under stirring to saturate the solution verified by closing the valve from time to time and observing whether the pressure remained constant. When the set pressure remained constant, stirring was stopped and $H_2$ was added rapidly reaching saturation. The autoclave was then heated and the pressure monitored with digital pressure gauges connected to a PC. The pressure increases upon heating and it was waited till constant value before the reaction was started by switching on the stirring. Completion of the reaction was indicated by constant pressure after the pressure drop. The autoclave was then cooled to r.t. and the pressure was released carefully. The aqueous phase and organic phase were removed separately and analyzed by $^1$H-NMR as described above.

### $CO_2$ hydrogenation in presence of basic amino acids and Ru-dppm in MIBC/$H_2O$ system

The reactions were carried out as described above using an aqueous solution (3 mL, 0.86 M) of arginine (Arg) or lysine (Lys) or an aqueous solution (3 mL, 0.25 M) histidine (His), respectively, and a solution of Ru-dppm (2 mL, 0.5 mM) dissolved in degassed methyl isobutyl carbinol (MIBC) as the catalyst phase. The obtained amounts of formic acid (n(FA)), the formic acid-base ratio (FA/Base), the turnover number (TON) and the initial turnover frequency ($TOF_{ini}$) are shown in Table S1.

*Table S1: $CO_2$ Hydrogenation in presence of basic amino acids and Ru-dppm in MIBC/$H_2O$.*

| Entry | Amino Acid | n(FA) [mmol] | FA/Base [-] | TON [-] | $TOF_{ini}$ [$h^{-1}$] |
|---|---|---|---|---|---|
| 1 | Arginine | 2.376 | 0.895 | 2286 | 23744 |
| 2 | Histidine | 0.821 | 1.108 | 824 | 1769 |
| 3 | Lysine | 1.285 | 0.467 | 1306 | 1972 |

In Figure S3 the respective smoothed pressure-time curves are displayed.

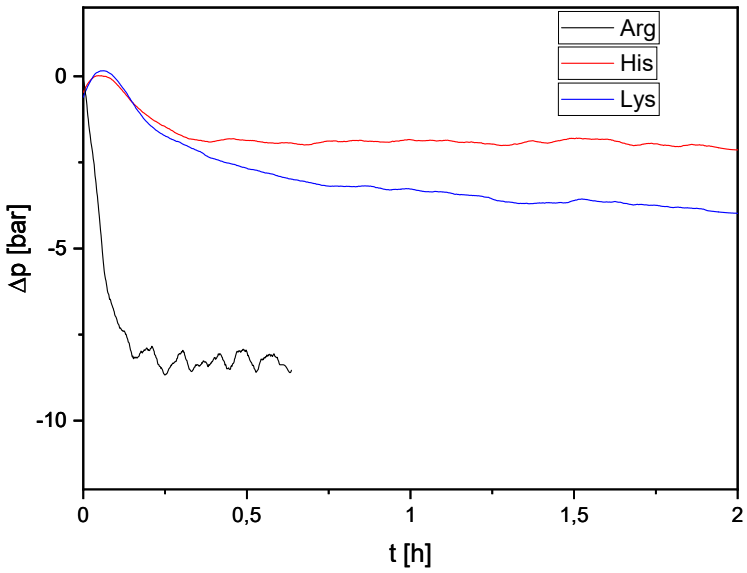



*Figure S3: Pressure-time curves for the $CO_2$ Hydrogenation in presence of basic amino acids and Ru-dppm in MIBC/$H_2O$ system*

## $CO_2$ hydrogenation in presence of basic amino acids and Ru-$C_{12}$-dppm in tetradecane /$H_2O$

The reactions were carried out as described above using Ru-$C_{12}$-dppm as the catalyst and tetradecane as the catalyst phase. The results are shown in Table S2.

*Table S2: $CO_2$ Hydrogenation in presence of basic amino acids and Ru-$C_{12}$-dppm in tetradecane/$H_2O$*

| Entry | Amino Acid | n(FA) [mmol] | FA/Base [-] | TON [-] | $TOF_{ini}$ [$h^{-1}$] |
|---|---|---|---|---|---|
| 1 | Arginine | 2.663 | 1.016 | 2659 | 329 |
| 2 | Histidine | 0.766 | 1.069 | 749 | 92 |
| 3 | Lysine | 0.100 | 0.036 | 101 | - |

The respective smoothed pressure-time curves are displayed in Figure S4.

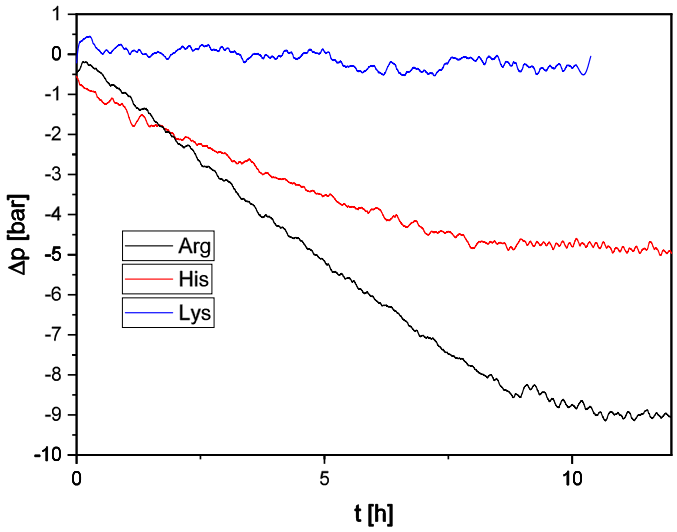



*Figure S4: Pressure-time curves for the $CO_2$ Hydrogenation in presence of basic amino acids and Ru-$C_{12}$-dppm in tetradecane.*

## $CO_2$ hydrogenation in presence of Arg and Ru-$C_{12}$-dppm in various apolar solvents /$H_2O$

The reactions were carried out as described above using Ru-$C_{12}$-dppm as the catalyst in the presence of Arg and different organic solvents as the catalyst phase. The obtained parameters are shown in Table S3.

*Table S3: $CO_2$ Hydrogenation in presence of arginine and Ru-$C_{12}$-dppm in different solvents.*

| Entry | Solvent | n(FA) [mmol] | FA/Base [-] | TON [-] | $TOF_{ini}$ [$h^{-1}$] | c(solvent)[a] [g $L^{-1}$] |
|---|---|---|---|---|---|---|
| 1 | 1-Hexanol | 2.67 | 0.96 | 2516 | 229 | 5.35 |
| 2 | MIBC | 2.50 | 0.91 | 2530 | 2827 | 11.04 |
| 3 | 3-Methylbutanone | 1.43 | 0.52 | 1402 | 1718 | 35.56 |
| 4 | 1-Octanol | 2.44 | 0.89 | 2423 | 2505 | 0.39 |
| 5 | Isooctanol | 2.76 | 0.99 | 2790 | 8346 | 1.5 |
| 6 | 2-MTHF | 2.55 | 0.79 | 2475 | 14163 | 49.05 |
| 7 | Ethylacetate | 2.21 | 0.81 | 1971 | 26367 | 40.91 |
| 8 | 1-Dodecanol | 2.59 | 0.94 | 2600 | 11824 | <0.1 |
| 9 | Anisole | 2.61 | 0.94 | 2675 | 5216 | 1.33 |
| 10 | Hexylhexanoate | 2.96 | 1.06 | 2915 | 1372 | <0.1 |
| 11 | *n*-Octylacetate | 3.15 | 1.13 | 2761 | 3614 | <0.1 |
| 12 | Toluene | 2.49 | 0.91 | 2404 | 458 | 1.39 |
| 13 | Tetreadecane | 2.66 | 1.02 | 2659 | 329 | <0.1 |

[a] Concentration of the respective solvent in the aqueous phase after catalysis, determined by quantitative $^{1}$H-NMR.

In Figure S5 the respective smoothed pressure-time curves are displayed.

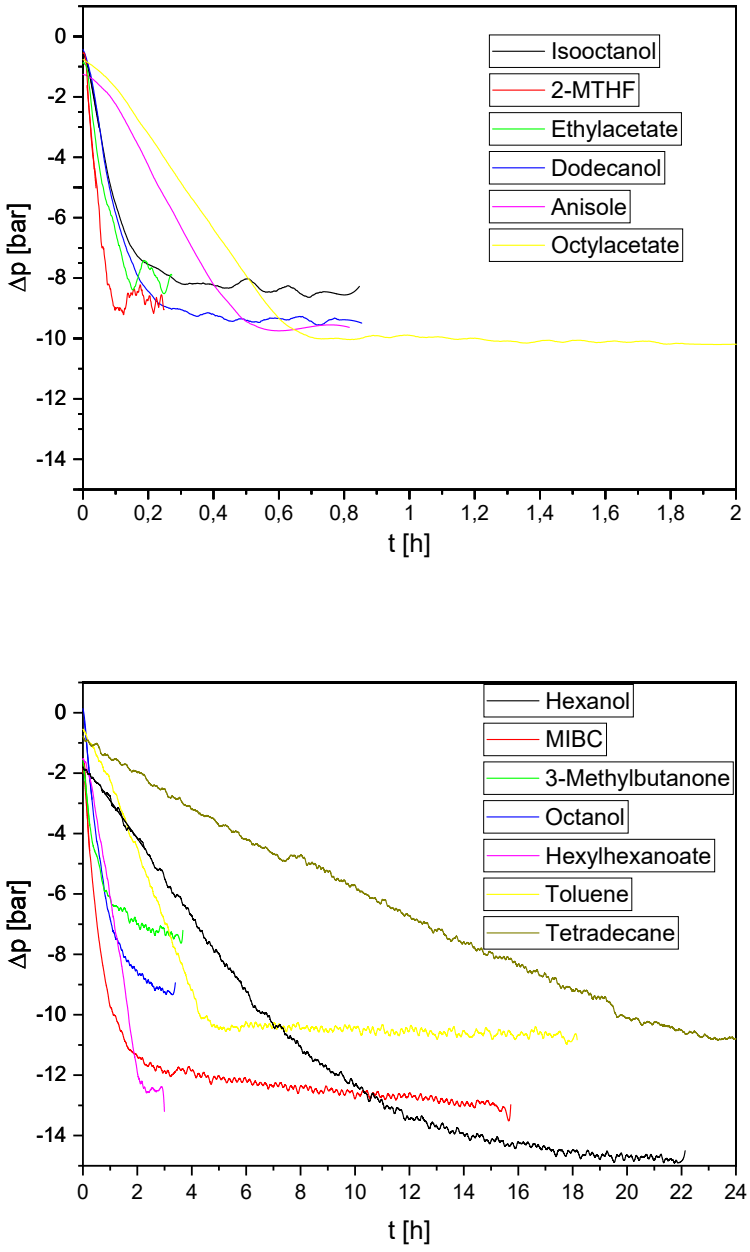



*Figure S5: Pressure-time curves for the $CO_2$ Hydrogenation in presence of basic amino acids and Ru-$C_{12}$-dppm in various solvents*

## Correlation of $TOF_{ini}$ for the examined solvents with their characteristic parameters

*Table S4: $TOF_{ini}$, dielectric constant ($\varepsilon$), log(P), $E_t(30)$-value, Kamlet-Taft solvent parameters $\beta$ and $\pi$, donor number, $CO_2$ solubility and $H_2$ solubility for the examined catalyst phases. Sometimes values from similar compounds are given because of missing literature values.*

| Solvent | $TOF_{ini}$ [$h^{-1}$] | $\varepsilon$[3] | logP[3] | $E_T(30)$[4] [kcal $mol^{-1}$] | $\beta$[5] | $\pi$[5] | DN[6] [kcal $mol^{-1}$] | $X(CO_2)$[3] | $X(H_2)$[3] [x $10^4$] |
|---|---|---|---|---|---|---|---|---|---|
| Hexanol | 229 | 13.03 | 2.03 | 48.8 | 0.84 | 0.4 | 30 | 0.0108 | |
| MIBC | 2827 | 10.4 | 1.7 | | | | | | |
| 3-Methylbutanone | 1718 | 10.37 | 0.56 | 40.9 | 0.48[d] | 0.67[d] | 16 | | |
| Octanol | 2505 | 10.3 | 3.07 | 48.1 | 0.081 | 0.4 | 32 | 0.00938 | 3.92 |
| Isooctanol | 8346 | 7.58 | | | | | | | |
| 2-Methyl-tetrahydrofuran (2-MTHF) | 14163 | 6.97 | 1.85 | 37.4[b] | 0.55[b] | 0.58[b] | 18 | 0.027 | 2.7 |
| Ethylacetate | 26367 | 6.08 | 0.73 | 38.1 | 0.45 | 0.55 | 17.1 | 0.023 | 2.46 |
| Dodecanol | 11824 | 5.82 | 5.13 | 47.5 | | | 31[e] | 0.01664 | 3.7 |
| Anisole | 5216 | 4.3 | 2.11 | 37.1 | 0.22 | 0.73 | 9 | | |
| Hexylhexanoate | 1372 | 4.22 | 4.7 | | | | | | |
| Octylacetate | 3614 | 4.18 | 3.4 | 38.5[c] | 0.45[c] | 0.46[c] | 15[c] | | |
| Toluene | 458 | 2.38 | 2.73 | 33.9 | 0.11 | 0.54 | 0.1 | 0.0113 | 3.4 |
| Tetradecane | 329 | 2.03 | 7.2 | 31.1[a] | 0[a] | -0.08[a] | 0[a] | 0.01361 | 6.8 |

[a]Hexane, [b]THF, [c]Butylacetate, [d]2-Butanone, [e]Decanol

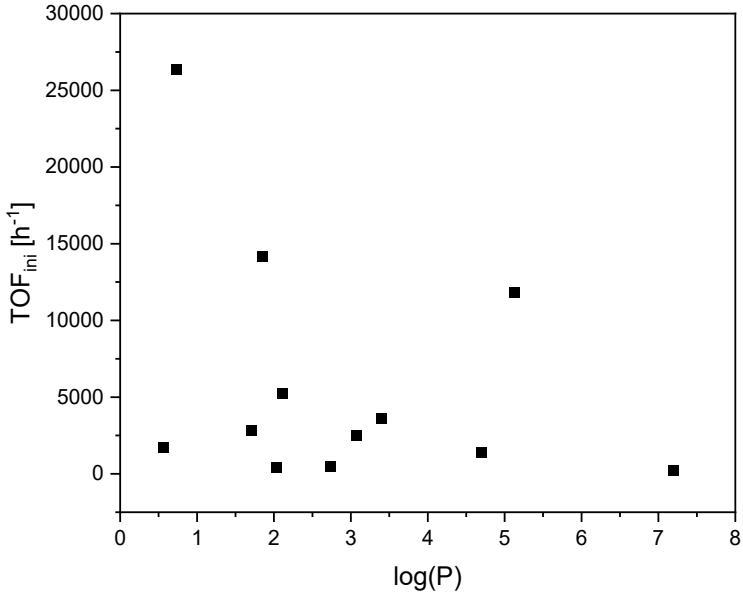



*Figure S6: Plot of log(P) vs $TOF_{ini}$.*

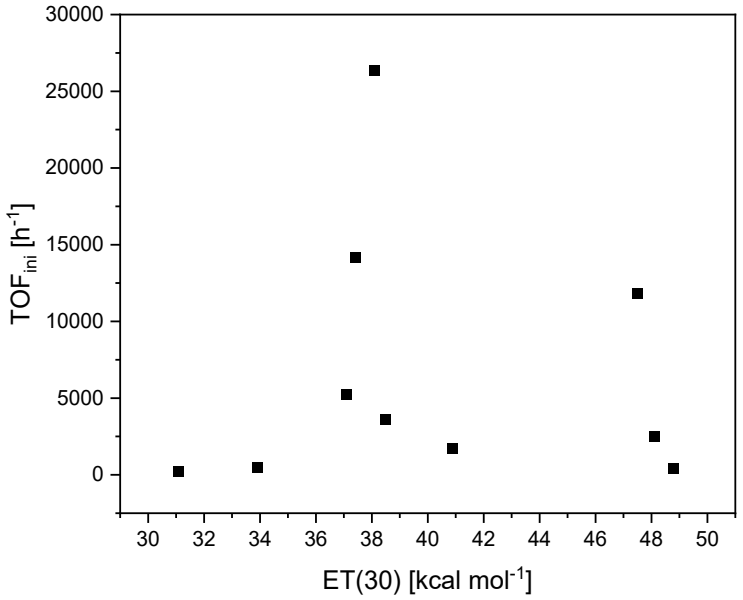



*Figure S7: Plot of ET(30) vs $TOF_{ini}$.*

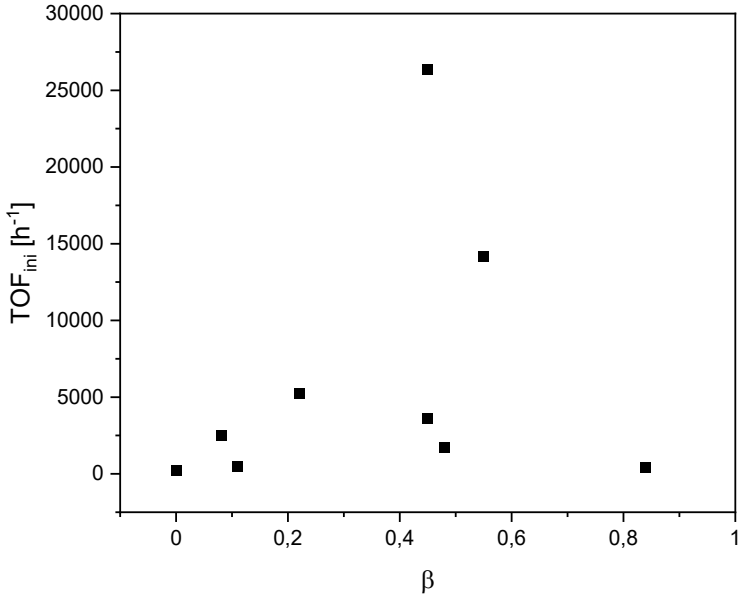



*Figure S8: Plot of the Kamlet-Taft parameter $\beta$ vs $TOF_{ini}$.*

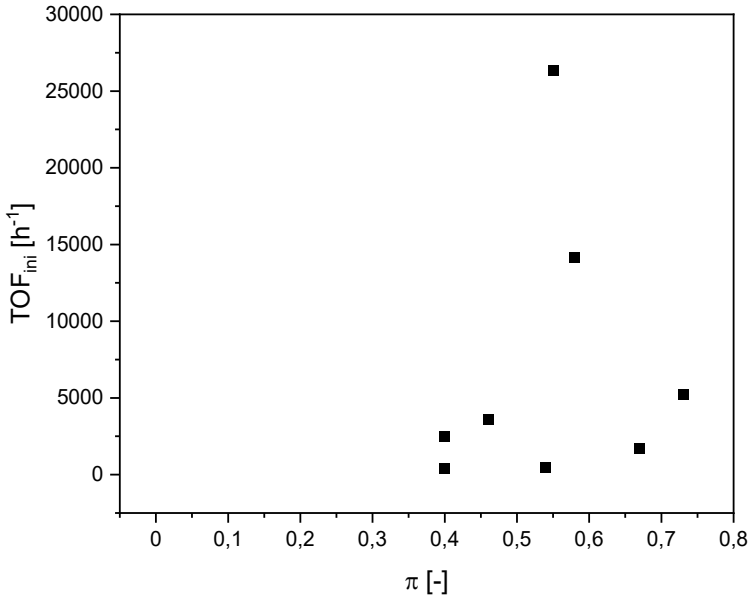



*Figure S9: Plot of the Kamlet-Taft parameter $\pi$ vs $TOF_{ini}$.*

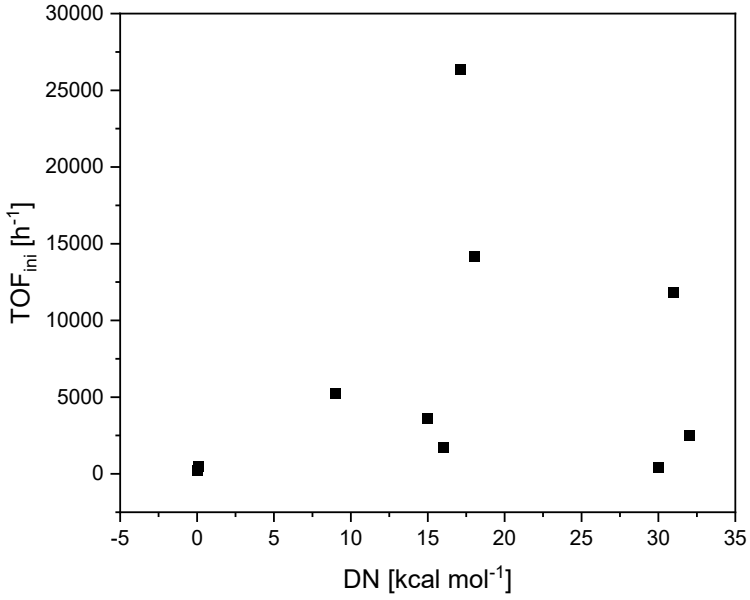



*Figure S10: Plot of DN vs $TOF_{ini}$.*

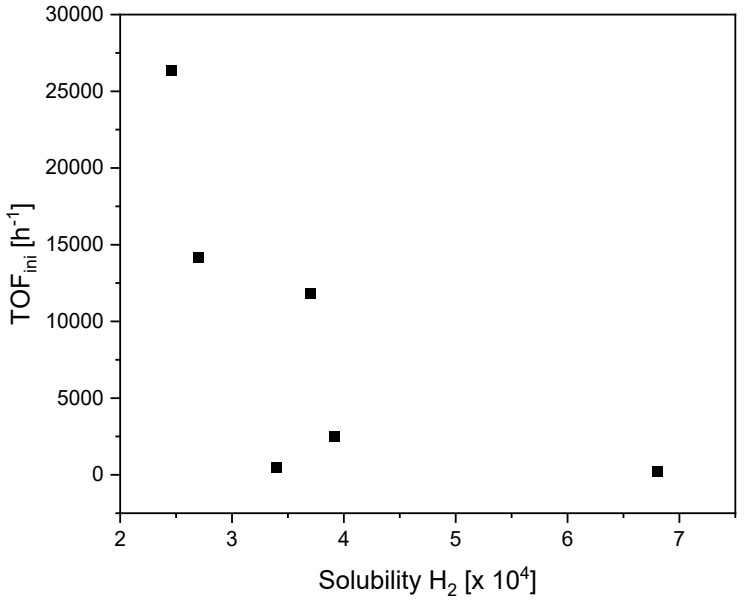



*Figure S11: Plot of the $H_2$-solubility vs $TOF_{ini}$.*

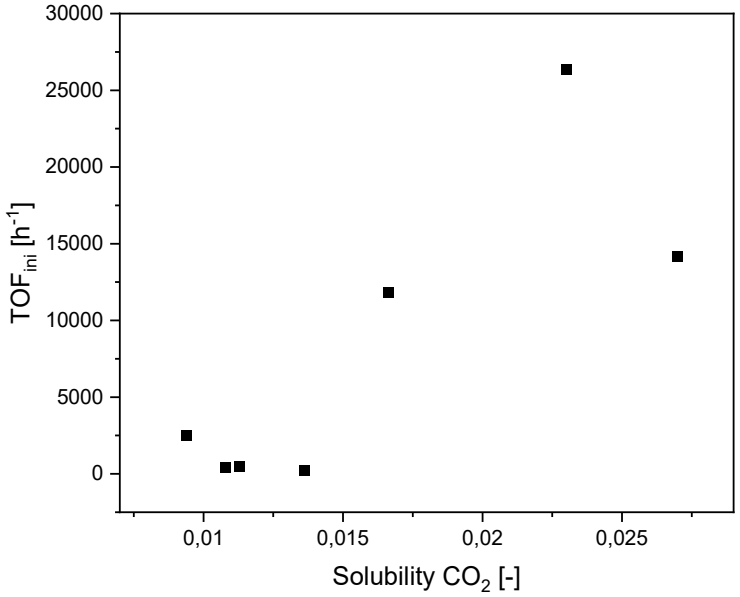



*Figure S12: Plot of the $CO_2$-solubility vs $TOF_{ini}$.*

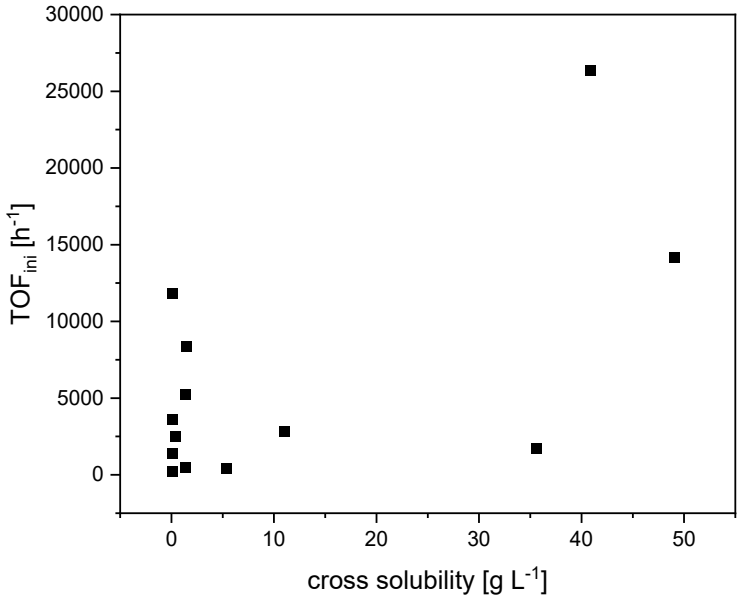



*Figure S13: Plot of the detected solvent cross-solubility vs $TOF_{ini}$.*

## $CO_2$ hydrogenation in the presence of Arg at different Ru-$C_{12}$-dppm loadings in tetradecane/$H_2O$ and 2-MTHF/$H_2O$

The reactions were carried out as described above in the presence of Arg in tetradecane/$H_2O$ or 2-MTHF/$H_2O$ using Ru-$C_{12}$-dppm at different loading. The obtained initial TOFs are depicted in Figure S14.

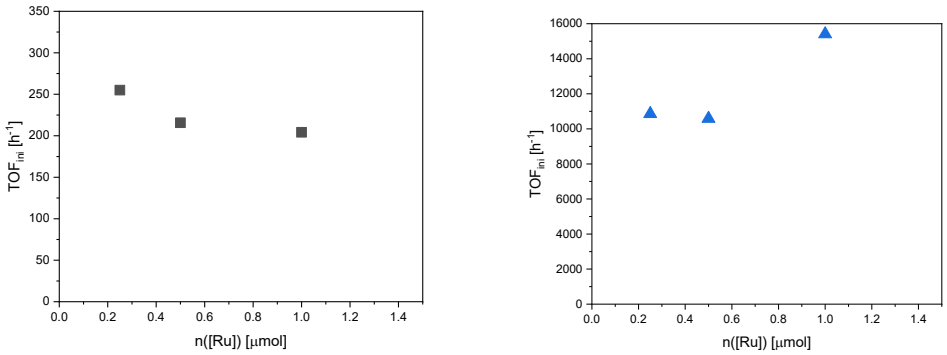



*Figure S14: $TOF_{ini}$ in correlation to the catalyst concentration for Ru-$C_{12}$-dppm in tetradecane (left) and 2-MTHF (right).*

## $CO_2$ Hydrogenation in the presence of Ru-$C_{12}$-dppm in dodecanol/$H_2O$ at different Arg loadings

Solid arginine (0.6827 g, 1.4074 g, 2.1041 g, 2.7696 g) was weighed into the autoclave, which was then degassed as described above. Degassed water (2 mL) was added resulting in 2, 4, 6 and 8 M solutions, respectively, when completely dissolved. A solution of Ru-$C_{12}$-dppm (2 mL, 0.5 mM) dissolved in degassed *n*-dodecanol was introduced in argon counterflow. With increasing amounts of arginine, the saturation with $CO_2$ took longer (e.g. up to 30 minutes for the 8 M solution). The reaction was carried out as described above. The obtained results are shown in Table S5.

*Table S5: $CO_2$ Hydrogenation in presence different Arg concentrations with Ru-$C_{12}$-dppm in n-dodecanol/$H_2O$.*

| c(Arg) | $TOF_{ini}$ [$h^{-1}$] | TON | FA/Base |
|---|---|---|---|
| 2 M | 9479 | 3488 | 0.935 |
| 4 M | 11107 | 6314 | 0.862 |
| 6 M | 15345 | 8329 | 0.769 |
| 8 M | 6494 | 9913 | 0.635 |

The respective pressure-time curves are shown in Figure S15.

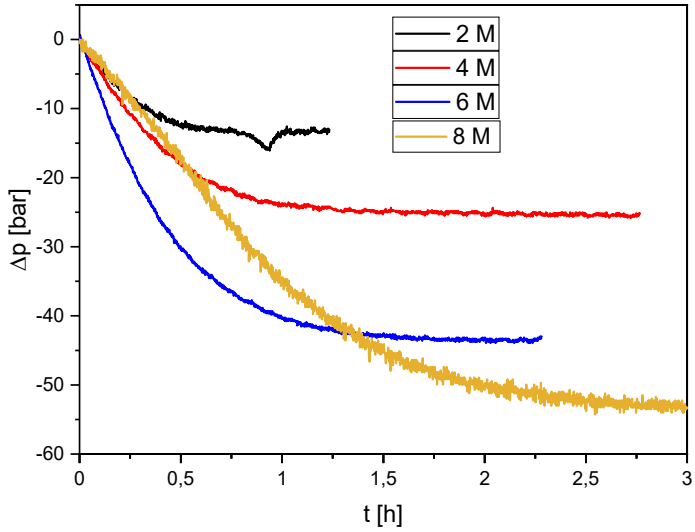



*Figure S15: Pressure-time curves of the $CO_2$ hydrogenation in presence different Arg concentrations with Ru-$C_{12}$-dppm in n-dodecanol/$H_2O$.*

Additionally, photographs of the mixtures before reaction (left), after saturation with $CO_2$ (middle) and after the reaction (right) are shown in Figure S16.

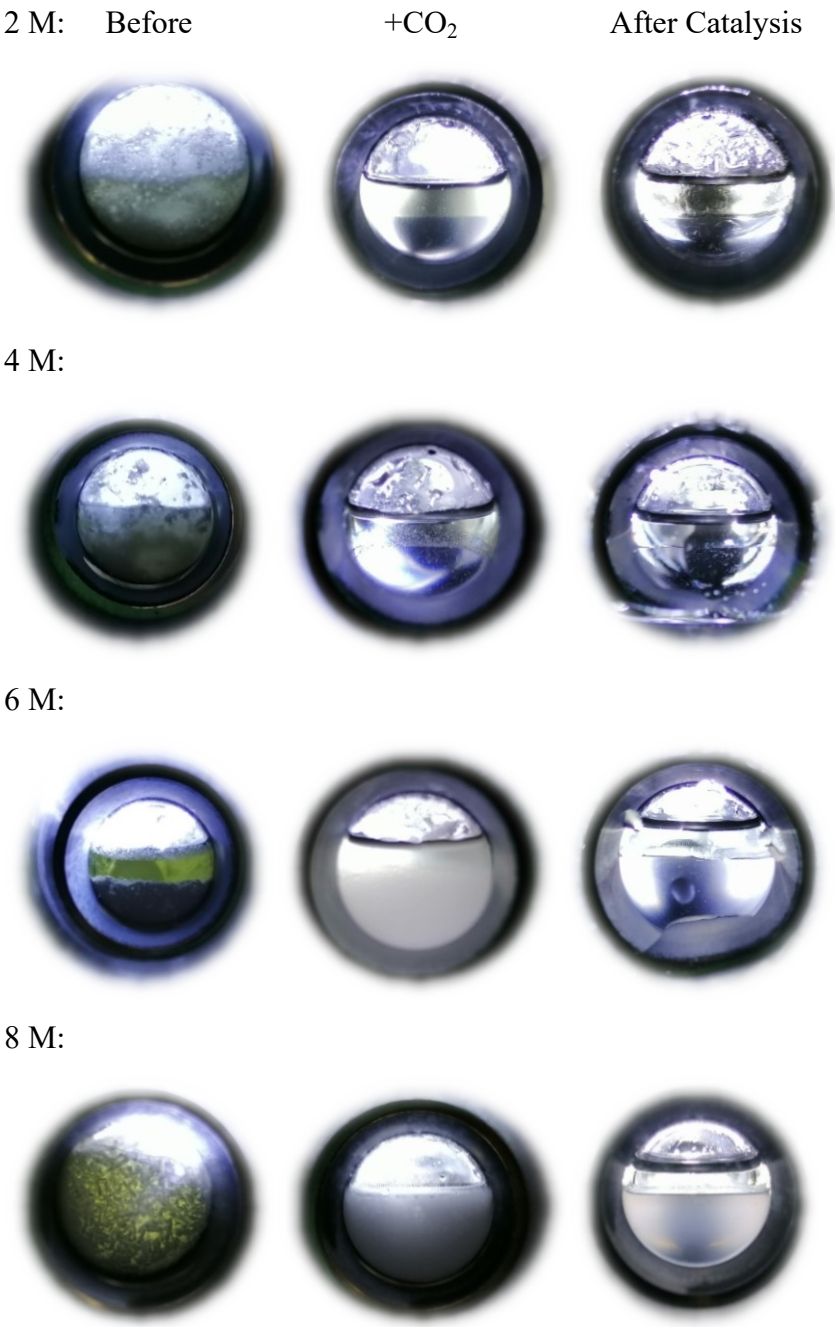



*Figure S16: Photographs of the mixtures before reaction (left), after saturation with $CO_2$ (middle) and after the reaction (right) for each Arg concentration.*

**Semi-continuous setup components**

High pressure reactions were carried out in stainless steel window autoclaves built and maintained by the mechanical workshop of the *Institute für Technische und Makromolekulare Chemie* of RWTH Aachen University. A semi-continuous reaction setup was established previously (Figure S17).[7]

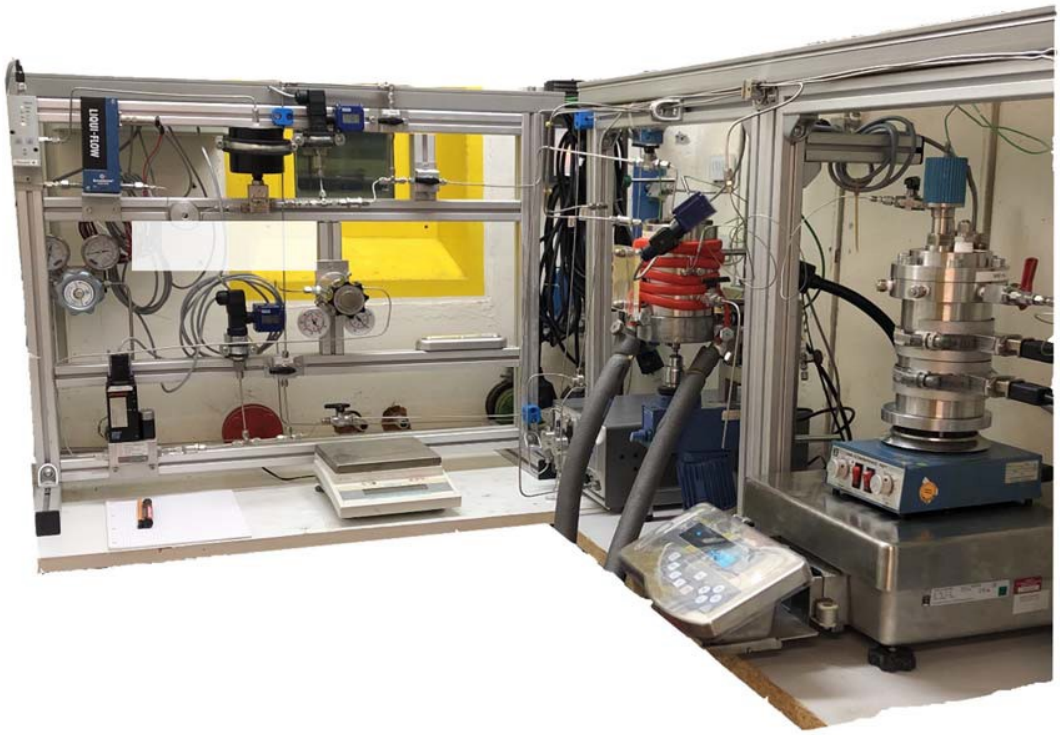



*Figure S17:* Picture of the semi-continuous plant.

A 100 mL window autoclave equipped with a gas- and substrate inlet and a digital pressure sensor at the top was used as the reactor (Figure S18). At the bottom there was an integrated heater, a mechanical stirrer, and a fine dosing valve for the product removal. The stirrer drove a magnetic agitator shaft, which drove the magnetic stir bar inside the autoclave. For the controlled $H_2$-addition, a commercial mass flow controller (Brooks Smart Mass Flow 5800, 150 $mL_N$ $min^{-1}$) was used.

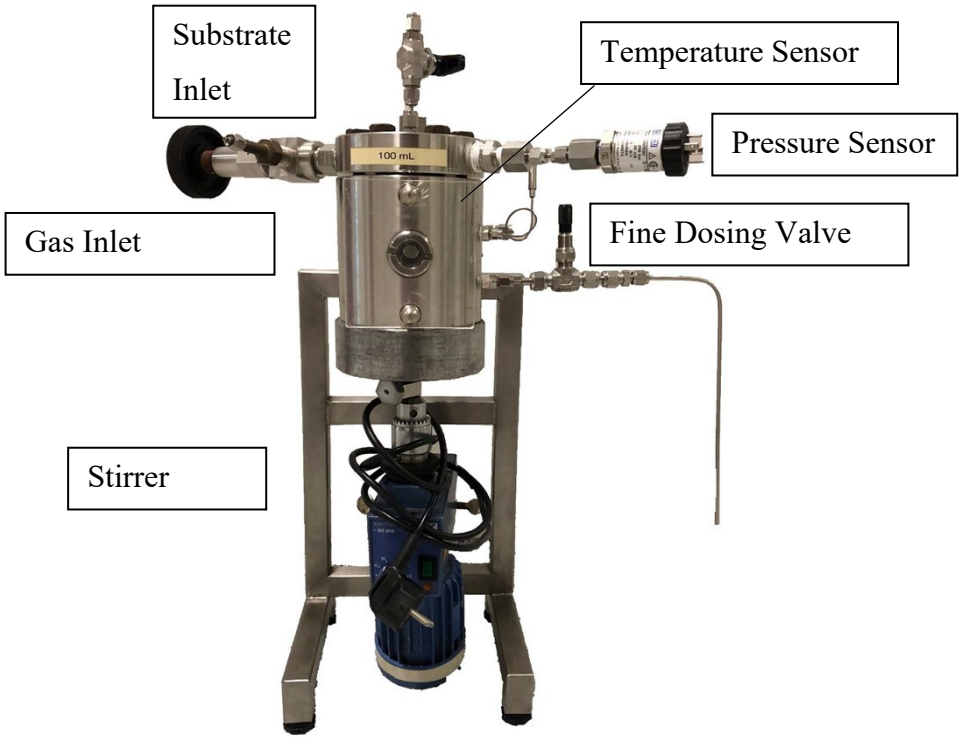



*Figure S18: Picture of the used 100 mL window autoclave.*

The 900 mL high pressure reservoir (Figure S19) was equipped with an outlet *via* a dip tube, a digital pressure sensor and a gas inlet valve standing on a precision scale (KERN FEJ Präzisionswaage).

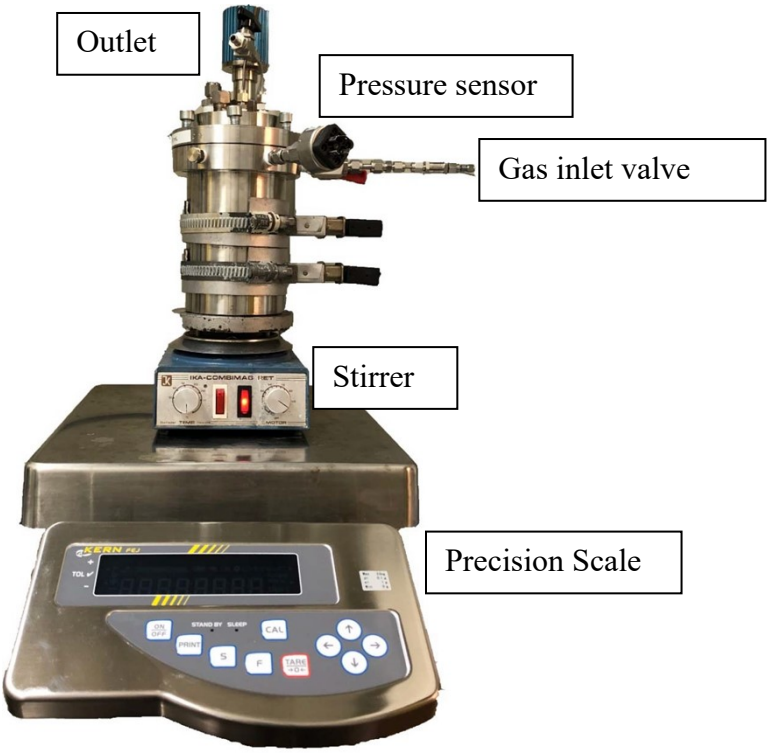



*Figure S19: Picture of the used 900 mL high pressure reservoir.*

## Recycling experiments in the semi-continuous setup

*Table S6: Repetitive hydrogenation of $CO_2$ in the semi-continuous setup. Conditions: see main manuscript.*

| Entry | t [h] | n(FA) [mmol] | $n(H_2)$ [mmol] | TON | $TOF_{ini}$ [$h^{-1}$] | FA/Base |
|---|---|---|---|---|---|---|
| 1 | 6 | 77.654 | 78.389* | 7 723 | 3212 | 0.893 |
| 2 | 6 | 88.286 | 84.962 | 8 780 | 3357 | 0.917 |
| 3 | 6 | 98.140 | 97.032 | 9 760 | 2881 | 0.926 |
| 4 | 6 | 99.793 | 94.743 | 9 924 | 2651 | 0.943 |
| 5 | 7.5 | 97.272 | 94.189 | 9 674 | 2395 | 0.926 |
| 6 | 7.5 | 109.233 | 111.156 | 10 863 | 2463 | 0.893 |
| 7 | 9 | 118.871 | 114.058 | 11 822 | 2873 | 0.935 |
| 8 | 8.5 | 110.106 | 97.107 | 10 950 | 2097 | 0.826 |
| 9 | 14.5 | 112.448 | 110.255 | 11 183 | 1871 | 0.909 |
| 10 | 24 | 116.668 | 101.005 | 11 603 | 1217 | 0.893 |
| Sum | - | 1028.471 | 983 | 102 282 | - | - |

*Autoclave not completely tight: values corrected by 2.5 mL $min^{-1}$ leakage

*Table S7: Catalyst leaching determined by ICP-MS for the recycling experiments.*

| Run | Ruthenium leaching in the aqueous phase | |
|---|---|---|
| | [ppm] | [%] |
| 1 | 0.496 | 2.132 |
| 2 | 0.077 | 0.344 |
| 3 | 0.020 | 0.098 |
| 4 | 0.016 | 0.080 |
| 5 | 0.011 | 0.053 |
| 6 | 0.022 | 0.112 |
| 7 | 0.024 | 0.120 |
| 8 | 0.017 | 0.084 |
| 9 | 0.020 | 0.095 |
| 10 | 0.039 | 0.095 |
| Sum | | 3.326 |

# References


[1] M. Scott, B. Blas Molinos, C. Westhues, G. Franciò, W. Leitner, *ChemSusChem* **2017**, *10*, 1085.

[2] M. Scott, C. G. Westhues, T. Kaiser, J. C. Baums, A. Jupke, G. Franciò, W. Leitner, *Green Chem.* **2019**, *21*, 6307.

[3] David R. Lide, *CRC Handbook of Chemistry and Physics*. *Internet Version 2005*, CRC Press, Boca Raton, FL, **2005**.

[4] C. Reichardt, T. Welton, *Solvents and solvent effects in organic chemistry*, Wiley-VCH, Weinheim, **2011**.

[5] M. J. Kamlet, J.- L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.* **1983**, *48*, 2877.

[6] F. Cataldo, *Eur. Chem. Bull.* **2015**, *4(2)*, 92.

[7] W. Leitner, G. Franciò, M. Scott, C. Westhues, J. Langanke, M. Lansing, C. Hussong, E. Erdkamp, *Chem. Ing. Tech.* **2018**, *90*, 1504.