

Supporting Information

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Continuous-Flow Hydrogenation of Carbon Dioxide to Pure Formic Acid using an Integrated scCO₂ Process with Immobilized Catalyst and Base**

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1) General

Safety advice: High-pressure experiments with compressed gases represent a significant safety risk and should only be conducted in conjunction with the use of suitable equipment.

Where needed, moisture and oxygen were excluded by working in a glovebox or by using Schlenk techniques. Argon 4.8 (Messer, Germany) was used as inert gas. Glassware was dried at 400 °C with a heat gun, evacuated and backfilled with argon at least three times. All solvents were purified by distillation prior to use. Dichloromethane was degassed by bubbling argon through it and dried by passing it over activated alumina in steel columns. Acetonitrile was degassed by bubbling argon through it and stored over activated molecular sieves. Deionised water was obtained from a reverse-osmotic purification system (Werner Easy Pure II). All reagents were commercially supplied by Aldrich, Fluka, Alfa Aesar or Iolitec and used as received unless stated otherwise. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Iolitec) was degassed and dried in high vacuum at 70 °C for 48 h. Triethylamine and tetramethylethylenediamine (Aldrich) were distilled under argon and stored over molecular sieves under argon. 1,2-Dimethylimidazole (Aldrich) was recrystallised from toluene and stored under argon. Reaction gases hydrogen (grade 5.0) and carbon dioxide (grade 4.6) were supplied by Linde and PraxAir and used without further purification. QuadraPure™-DMA was donated by Johnson Matthey.

2) Analyses

NMR spectra were recorded with commercial spectrometers Bruker AV-600, AV-400 or AV-300 at room temperature in deuterated solvents. Chemical shifts δ are given in ppm relative to tetramethylsilane (^1H and ^{13}C) and 85 % phosphoric acid (^{31}P). First order spin multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quadruplet (qua), quintet (qui), sextet (sext) and septet (sep). Couplings of higher order or overlapped signals are denoted as multiplet (m), broadened signals as (br). First order coupling constants J are given in Hz. Assignments are based on attached proton tests (APT) and 2-D correlation spectroscopy (HSQC, HMQC, HMBC).

Molecular masses of compounds were determined by electrospray ionisation mass spectrometry (ESI-MS) on a Varian 500 MS.

3) Syntheses of non-volatile bases

1-(*N,N*-Diethylaminoethyl)-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (**5**)

The protocol is based on a modified literature procedure.¹

1,2-Dimethylimidazole (0.2 mol, 19.23 g) and 2-chloro-*N,N*-diethylethylamine hydrochloride (0.2 mol, 34.42 g) were combined in acetonitrile (200 mL) and refluxed for 93 hours under argon. After cooling to room temperature (RT), the mixture was filtered and the remaining white solid washed with acetonitrile (100 mL) and acetonitrile/Et₂O (1:1, 3 × 80 mL). After drying in vacuo, pure 1-(*N,N*-diethylaminoethyl)-2,3-dimethylimidazoliumchloride hydrochloride **12** was obtained as colourless solid (42.2 g, 79 %).

12 (21 mmol, 5 g) was dissolved in water (60 mL) and NaOH (20 mmol, 0.79 g) added at 0 °C. After stirring overnight at room temperature, all volatiles were removed in vacuo and the residue extracted with dichloromethane (60 mL). After filtration, the solvent was evaporated to give 1-(*N,N*-diethylaminoethyl)-2,3-dimethylimidazoliumchloride **13** as white powder (4.31 g, 90 %).

13 (21 mmol, 4.8 g) and lithium bis(trifluoromethylsulfonyl)imide (21 mmol, 5.94 g) were dissolved in water (15 mL). Dichloromethane (50 mL) was added and the mixture stirred for 1 hour. After separation, the aqueous phase was extracted with dichloromethane (20 mL). The combined organic phases were extracted with portions of water until addition of AgNO₃ (1 M) to the aqueous washing did not show any turbidity (8 × 10 mL). Drying in high vacuum (HV) for 24 hours at 60 °C yielded **5** as colourless, viscous liquid (7.78 g, 79 %). The residual water content by Karl-Fischer titration was 54 ppm.

¹H-NMR (400 MHz, CDCl₃): δ = 7.35 – 7.20 (m, 2H, NCHCHN), 4.06 (t, ³J(H,H) = 5.6 Hz, 2H, NCH₂CH₂N(CH₂CH₃)₂), 3.79 (s, 3H, NCH₃), 2.75 (t, ³J(H,H) = 5.6 Hz, 2H, NCH₂CH₂N(CH₂CH₃)₂), 2.61 (s, 3H, N₂CCH₃), 2.49 (q, ³J(H,H) = 7.2 Hz, 4H, NCH₂CH₂N(CH₂CH₃)₂), 0.88 (t, ³J(H,H) = 7.2 Hz, 6H, NCH₂CH₂N(CH₂CH₃)₂) ppm. ¹³C{¹H}-NMR (75 MHz, CDCl₃): δ = 144.3 (s, N₂CCH₃), 122.1 & 121.6 (s, NCHCHN), 119.9 (qua, ¹J(C,F) = 321 Hz, CF₃), 52.7 (s, NCH₂CH₂N(CH₂CH₃)₂), 47.6 (s, NCH₂CH₂N(CH₂CH₃)₂), 47.0 (s, NCH₂CH₂N(CH₂CH₃)₂), 35.2 (s, NCH₃), 11.6 (s, NCH₂CH₂N(CH₂CH₃)₂), 9.8 (s, N₂CCH₃) ppm. ¹⁹F{¹H}-NMR (282 MHz, CDCl₃): δ = -79.1 (s, CF₃) ppm.

ESI-MS (+): m/z = 196.3. ESI-MS (-): m/z = 280.1.

1-(*N,N*-Diethylaminoethyl)-2,3-dimethylimidazolium trifluoromethanesulfonate (6)

The protocol is based on a modified literature procedure.²

12 (21 mmol, 5.0 g) was dissolved in MeOH (60 mL) and NaOH (20 mmol, 0.79 g) was added at 0 °C. The solution was allowed to warm to room temperature, sodium trifluoromethanesulfonate (21 mmol, 3.63 g) was added and the mixture stirred overnight. MeOH was removed from the mixture in vacuo, dichloromethane (60 mL) was added and the mixture filtered after stirring for 2 hours. Drying in HV for 24 hours at 60 °C yielded **6** as slightly orange solid (5.87 g, 82 %).

¹H-NMR (400 MHz, *d*₆-DMSO): δ = 7.63 – 7.59 (m, 2H, NCHCHN), 4.14 (t, ³*J*(H,H) = 5.8 Hz, 2H, NCH₂CH₂N(CH₂CH₃)₂), 3.76 (s, 3H, NCH₃), 2.67 (t, ³*J*(H,H) = 5.8 Hz, 2H, NCH₂CH₂N(CH₂CH₃)₂), 2.59 (s, 3H, N₂CCH₃), 2.45 (q, ³*J*(H,H) = 7.2 Hz, 4H, NCH₂CH₂N(CH₂CH₃)₂), 0.83 (t, ³*J*(H,H) = 7.2 Hz, 6H, NCH₂CH₂N(CH₂CH₃)₂) ppm. **¹³C{¹H}-NMR** (100 MHz, *d*₆-DMSO): δ = 144.5 (s, N₂CCH₃), 122.0 & 121.3 (s, NCHCHN), 120.7 (qua, ¹*J*(C,F) = 322 Hz, CF₃), 52.1 (s, NCH₂CH₂N(CH₂CH₃)₂), 46.3 (s, NCH₂CH₂N(CH₂CH₃)₂), 39.5 (sep, *d*₆-DMSO & NCH₂CH₂N(CH₂CH₃)₂), 34.6 (s, NCH₃), 11.6 (s, NCH₂CH₂N(CH₂CH₃)₂), 9.3 (s, N₂CCH₃) ppm. **¹⁹F{¹H}-NMR** (376.5 MHz, *d*₆-DMSO): δ = -77.8 (s, CF₃) ppm.

ESI-MS (+): *m/z* = 196.3. **ESI-MS (-):** *m/z* = 149.0.

1-(*N,N*-Diethylaminoethyl)-2,3-dimethylimidazolium formate (7)

The synthesis of **7** was done by a literature known method.³ Ion exchange of **13** (19 mmol, 4.31 g) dissolved in water (5 mL) was done by passing the solution through a column filled with Ambersep 900-OH (78 g). The resulting OH⁻ salt was neutralised with formic acid (19 mmol, 856 mg). Evaporation of the water in vacuo and drying in HV for 24 hours at 60 °C yielded **7** as white solid (3.74 g, 84 %). Quantitative ion exchange was confirmed by NMR.

¹H-NMR (400 MHz, D₂O): δ = 8.42 (s, 1H, HCO₂), 7.39 – 7.32 (m, 2H, NCHCHN), 4.24 (t, ³*J*(H,H) = 7.2 Hz, 2H, NCH₂CH₂N(CH₂CH₃)₂), 3.75 (s, 3H, NCH₃), 2.93 (t, ³*J*(H,H) = 7.2 Hz, 2H, NCH₂CH₂N(CH₂CH₃)₂), 2.65 (q, ³*J*(H,H) = 7.2 Hz, 4H, NCH₂CH₂N(CH₂CH₃)₂), 2.59 (s, 3H, N₂CCH₃), 1.03 (t, ³*J*(H,H) = 7.2 Hz, 6H, NCH₂CH₂N(CH₂CH₃)₂) ppm. **¹³C{¹H}-NMR** (75 MHz, D₂O): δ = 170.8 (s, HCO₂), 144.5 (s, N₂CCH₃), 122.5 & 120.6 (s, NCHCHN), 50.5 (s, NCH₂CH₂N(CH₂CH₃)₂), 46.7 (s, NCH₂CH₂N(CH₂CH₃)₂), 44.8 (s, NCH₂CH₂N(CH₂CH₃)₂), 34.6 (s, NCH₃), 9.9 (s, NCH₂CH₂N(CH₂CH₃)₂), 8.9 (s, N₂CCH₃) ppm.

ESI-MS (+): *m/z* = 196.2. **ESI-MS (-):** Outside detection range (< *m/z* = 50).

1-(*N,N*-Diisopropylaminoethyl)-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide (**8**)

1,2-Dimethylimidazole (53 mmol, 5.07 g) and 2-diisopropylaminoethylchloride hydrochloride (53 mmol, 10.54 g) were combined in acetonitrile (60 mL) and refluxed for 5 days under argon. After cooling to RT, the resulting precipitate was separated by filtration and washed with acetonitrile (3 × 5 mL) and diethyl ether (2 × 10 mL). Drying in HV yielded a white solid (12.46 g, 80%). 6.23 g (21 mmol) of this solid were dissolved in water (50 mL) and NaOH (20 mmol, 0.80 g) was added at 0°C. After stirring overnight, the amount of water was reduced in vacuo to 15 mL. Lithium bis(trifluoromethylsulfonyl)imide (21 mmol, 6.04 g) and dichloromethane (50 mL) were added and the mixture stirred for 30 minutes at RT. After separation, the aqueous phase was extracted with dichloromethane (20 mL). The combined organic phases were washed with portions of water until addition of AgNO₃ (1 M) to the aqueous washing did not show any turbidity (11 × 15 mL). After removing of dichloromethane in vacuo and drying in HV at 70 °C for 24 hours, **8** was obtained as colourless liquid which crystallised after several hours to yield a white solid (9.85 g, 93 %).

¹H-NMR (400.2 MHz, CDCl₃): δ = 7.25 – 7.17 (m, 2H, NCHCHN), 4.06 (t, ³J(H,H) = 6.0 Hz, 2H, NCH₂CH₂N[CH(CH₃)₂]₂), 3.77 (s, 3H, NCH₃), 3.01 (sep, ³J(H,H) = 6.4 Hz, 2H, NCH₂CH₂N[CH(CH₃)₂]₂), 2.82 (t, ³J(H,H) = 6.0 Hz, 2H, NCH₂CH₂N[CH(CH₃)₂]₂), 2.62 (s, 3H, N₂CCH₃), 0.91 (d, ³J(H,H) = 6.4 Hz, 12H, NCH₂CH₂N[CH(CH₃)₂]₂) ppm. ¹³C{¹H}-NMR (100.6 MHz, CDCl₃): δ = 144.3 (s, N₂CCH₃), 122.4 & 122.0 (s, NCHCHN), 119.8 (qua, ¹J(C,F) = 321 Hz, CF₃), 49.2 (s, NCH₂CH₂N[CH(CH₃)₂]₂), 49.0 (s, NCH₂CH₂N[CH(CH₃)₂]₂), 45.2 (s, NCH₂CH₂N[CH(CH₃)₂]₂), 35.5 (s, NCH₃), 20.4 (s, NCH₂CH₂N[CH(CH₃)₂]₂), 10.2 (N₂CCH₃) ppm. ¹⁹F{¹H}-NMR (376.5 MHz, CDCl₃): δ = -78.9 (s, CF₃) ppm.

ESI-MS (+): m/z = 224.2. ESI-MS (-): m/z = 280.0.

1-Trimethylammonium-2-dimethylaminoethane bis(trifluoromethylsulfonyl)imide (**9**)

Tetramethylethylenediamine (0.5 mol, 58.11 g) was dissolved in dichloromethane (100 mL) and cooled to -78°C. Under stirring, methyl iodide in dichloromethane (0.5 mol, 70.97 g in 50 mL) was added over 30 minutes with a dropping funnel. After stirring at -78°C for 1 h, the mixture was allowed to warm to room temperature over 2 hours, resulting in the formation of a colourless precipitate. The mixture was transferred into a filter with dichloromethane (100 mL), and the solid washed with dichloromethane (3 × 50 mL). Drying in vacuo yielded 1-trimethylammonium-2-dimethylaminoethane iodide (103.96 g, 80.5 %). 1-Trimethylammonium-2-dimethylaminoethane iodide (194 mmol, 50.0 g) and lithium bis(trifluoromethylsulfonyl)imide (194 mmol, 54.3 g) were dissolved in water (100 mL) and dichloromethane was added (300 mL). After phase separation, the

aqueous phase was extracted with dichloromethane (100 mL), and the combined organic phases washed with water (10 × 50 mL) until addition of AgNO₃ (1 M) to the aqueous washing did not show any turbidity. Drying in high vacuum for 24 hours yielded **9** as colourless, viscous liquid (78.45 g, 97 %).

¹H-NMR (400 MHz, *d*₆-acetone): δ = 3.66 (t, 2H, ³*J*(H,H) = 5.9 Hz, N⁺CH₂), 3.38 (s, 9H, (CH₃)₃N⁺), 2.86 (m, 2H, (CH₃)₂NCH₂), 2.29 (s, 6H, (CH₃)₂N) ppm. ¹³C{¹H}-NMR (100 MHz, *d*₆-acetone): δ = 120.9 (qua, ¹*J*(C,F) = 321 Hz, CF₃), 63.6 (s, CH₂N⁺(CH₃)₃), 54.4 (s, CH₂N(CH₃)₂), 54.2 (s, N⁺(CH₃)₃), 45.1 (s, N(CH₃)₂) ppm. ¹⁹F{¹H}-NMR (376.50 MHz, *d*₆-acetone): δ = -79.88 (s) ppm.

ESI-MS(+): *m/z* = 131.3. ESI-MS (-): *m/z* = 280.2.

1,2-Dimethyl-3-propylimidazolium formate (**10**)

The synthesis of **10** was done by a literature known method.³ Ion exchange of 1,2-dimethyl-3-propylimidazolium iodide (24.4 mmol, 6.48 g) dissolved in water (5 mL) was done by passing the solution through a column filled with Ambersep 900-OH (78 g). The OH⁻ concentration of the resulting aqueous eluate was determined by titration with HCl (0.01 M) using bromothymol blue as indicator. The appropriate amount of formic acid (23 mmol, 1.07 g) dissolved in water (20 mL) was added, and the mixture stirred at room temperature overnight. Evaporation of the water in vacuo and drying in HV for 24 hours at 60 °C yielded **10** as slightly orange solid (4.24 g, 94 %). Quantitative ion exchange was confirmed by NMR. The residual water content by Karl-Fischer titration was 0.2 wt.-%.

¹H-NMR (400 MHz, *d*₆-DMSO): δ = 8.57 (s, 1H, HCO₂), 7.79 – 7.78 (m, 2H, NCHCHN), 4.10 (t, ³*J*(H,H) = 7.2 Hz, 2H, NCH₂CH₂CH₃), 3.78 (s, 3H, NCH₃), 2.60 (s, 3H, N₂CCH₃), 1.72 (sext, ³*J*(H,H) = 7.2 Hz, 2H, NCH₂CH₂CH₃), 0.85 (t, ³*J*(H,H) = 7.2 Hz, 3H, NCH₂CH₂CH₃) ppm. ¹³C{¹H}-NMR (100 MHz, *d*₆-DMSO): δ = 164.9 (s, HCO₂), 144.2 (s, N₂CCH₃), 122.4 & 121.0 (s, NCHCHN), 48.7 (s, NCH₂CH₂CH₃), 34.6 (s, NCH₃), 22.6 (s, NCH₂CH₂CH₃), 10.4 (s, NCH₂CH₂CH₃), 9.1 (s, N₂CCH₃) ppm.

4) Syntheses of IL-type ligands

1-Ethyl-2-methylimidazolium diphenyl(3-sulfonatophenyl)phosphine (EMIM TPPMS)

Sodium diphenyl(3-sulfonatophenyl)phosphine dihydrate (1.7 mmol, 672 mg) and 1-ethyl-2-methylimidazolium bromide (2 mmol, 382 mg) were dissolved in water (20 mL). Dichloromethane was added (20 mL) and the mixture gently shaken in a separating funnel. The emulsion was left at 4 °C overnight, yielding phase separation. After removal of the aqueous phase, water (20 mL) and more dichloromethane (10 mL) were added to the organic phase, and the emulsion left at 4 °C overnight. The procedure was repeated two more times. The organic phase was finally taken to dryness in vacuo yielding a waxy solid (416 mg, 55 %).

$^1\text{H-NMR}$ (400 MHz, d_6 -acetone): δ = 9.14 (s, 1H, N_2CH), 7.91 (d, $^3J(\text{H,P}) = 8.1$ Hz, 1H, sulfo-aryl- CH), 7.84 (d, $^3J(\text{H,P}) = 7.6$ Hz, 1H, sulfo-aryl- CH), 7.74 & 7.67 (2s, $2 \times 1\text{H}$, sulfo-aryl- CH), 7.44-7.22 (m, 12H, $\text{P}(\text{C}_6\text{H}_5)_2 + \text{NCHCHN}$), 4.34 (q, $^3J(\text{H,H}) = 7.3$ Hz, 2H, NCH_2CH_3), 4.00 (s, 3H, NCH_3), 1.52 (t, $^3J(\text{H,H}) = 7.3$ Hz, 3H, NCH_2CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (162 MHz, d_6 -acetone): δ = -5.18 (s) ppm.

Tetrabutylphosphonium diphenyl(3-sulfonatophenyl)phosphine (PBu_4TPPMS)

Sodium diphenyl(3-sulfonatophenyl)phosphine dihydrate (2.5 mmol, 1.00 g) and tetrabutylphosphonium chloride (2.5 mmol, 737 mg) were dissolved in water (30 mL). Dichloromethane was added (130 mL), and the mixture gently shaken in a separating funnel. The emulsion was left at 4 °C overnight yielding phase separation. After removal of the aqueous phase, water (30 mL) was added to the organic phase, and the emulsion left at 4 °C overnight. The procedure was repeated once more. The organic phase was taken to dryness in vacuo yielding a viscous, colourless liquid that crystallised after several days at room temperature (605 mg, 99 %).

$^1\text{H-NMR}$ (400 MHz, d_6 -acetone): δ = 7.95 (d, $^3J(\text{H,P}) = 8.0$ Hz, 1H, sulfo-aryl- CH), 7.93 (d, $^3J(\text{H,P}) = 7.9$ Hz, 1H, sulfo-aryl- CH), 7.40–7.15 (m, 12H, $\text{P}(\text{C}_6\text{H}_5)_2 + \text{sulfo-aryl-CH}$), 2.40 (m, 8H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.63 (m, 8H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.46 (q, $^3J(\text{H,H}) = 7.3$ Hz, 8H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.92 (t, $^3J(\text{H,H}) = 7.3$ Hz, 12H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) ppm. $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (162 MHz, d_6 -acetone): δ = 33.38 (s, PBu_4), -5.18 (s, TPPMS) ppm.

5) Formic Acid Analysis

HCO₂H was quantified on the basis of the relative integral value of the formyl proton in the ¹H-NMR compared to a known amount of 1,4-dioxane added as internal standard. Referencing of HCO₂H concentration against constant 0.1 M of 1,4-dioxane in acetone yielded a linear calibration factor of 1.21007±0.0234 (Figure 1). The standard deviation of the slope results in errors of ±2 %. Addition of the base NEt₃ to some mixtures did not influence the integral ratios. Using the calibration factor for determination of HCO₂H yields gave only small deviation (±4 %) from calculation of HCO₂H yields from weighed in 1,4-dioxane directly.

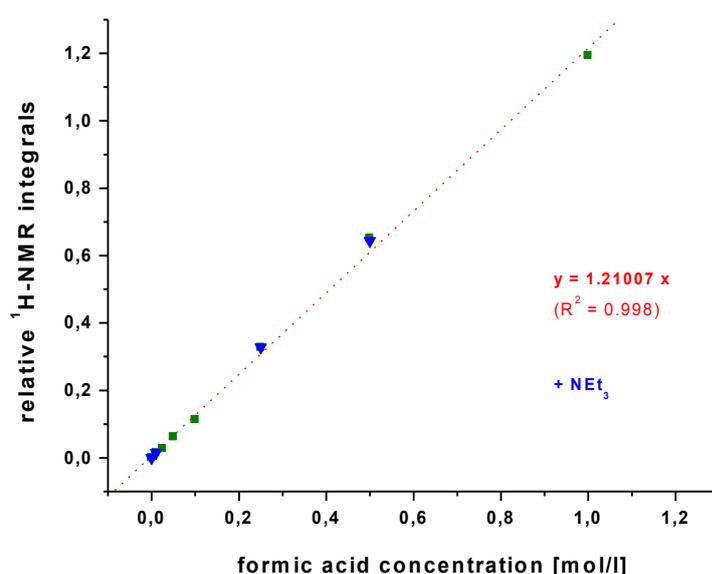


Figure 1. Calibration of formic acid concentration against 0.1 M 1,4-dioxane in acetone by ¹H-NMR integration (■ = pure HCO₂H, ▼ = with NEt₃ added).

The systematic limitations of NMR integration led to a somewhat larger error at the small concentrations detected in the early stage of the continuous-flow experiments. For appropriate integration all samples were measured with 256 scans and spectra were manipulated using TopSpin 3.0 (Bruker) (window function: type WDW = exponential, line broadening [Hz] = 1; zero filling to 64k). We have estimated the error to be 2–10 % as shown by concentration determinations of four reference samples with fixed concentrations in the critical range (Table 1). The reference samples were prepared as follows: HCO₂H and standard 1,4-dioxane were weighed into a volumetric flask, and water (8 mL) and *d*₆-acetone (2 mL) were added. After appropriate mixing, a sample of this mixture was analysed by ¹H-NMR as described above.

Table 1. Estimation of error in HCO₂H concentration determination by ¹H-NMR for low concentrated aqueous samples as obtained in continuous-flow experiments.^[a]

| Entry | Dioxane [mg] | HCO ₂ H added [mg] | HCO ₂ H determined [mg] | Deviation [%] |
|-------|--------------|-------------------------------|------------------------------------|---------------|
| 1 | 80.0 | 5.9 | 5.3 | 9.6 |
| 2 | 82.9 | 6.7 | 6.2 | 7.7 |
| 3 | 87.3 | 12.1 | 11.4 | 5.4 |
| 4 | 92.0 | 17.6 | 17.2 | 2.3 |

[a] Conditions: HCO₂H and standard 1,4-dioxane were dissolved in 8 mL H₂O and 2 mL *d*₆-acetone and the amount of HCO₂H was determined by ¹H-NMR analysis of this mixture.

6) Batch catalysis experiments

All high pressure batch experiments were conducted in stainless steel autoclaves ($V = 12\text{--}13$ mL) equipped with sapphire windows and a magnetic stir bar. Prior to use, the autoclave was inertised by drying at 60 °C in HV and repeatedly backfilling with argon. For the experiments with QuadraPure™-DMA resin, the resin was weighed into the autoclave prior to the inertisation procedure. In a glove box a stock solution of the catalyst precursor and ligand was prepared in dichloromethane [$c(\text{metal}) = 8 \mu\text{mol/mL}$] and the desired amount transferred into a Schlenk-tube. In case of the insoluble [Ru(cod)Cl₂]_n the solid precursor was weighed in directly. If needed, an aliquot of a stock solution of 1-ethyl-3-methylimidazolium chloride in dichloromethane was added. Ionic liquid was added last, and the mixture stirred at 70 °C for 2 hours in high vacuum to remove dichloromethane. The final catalyst concentration was 2 $\mu\text{mol/mL}$ in all cases. The freshly prepared catalyst solution in ionic liquid was then transferred into the inertised autoclave via syringe. If needed, NEt₃ was added at this point. The autoclave was closed and heated to reaction temperature (typically 50 °C). CO₂ was pressurised first (50 bar), and the reaction started by adding H₂ up to a total pressure of 100 bar. After the reaction, the autoclave was placed in ice-water and carefully vented after cooling. About 1 mmol NMR-standard (88.1 mg 1,4-dioxane) was weighed into a graduated cylinder, the exact mass was noted, and 1 mL of *d*₆-acetone (or *d*₆-DMSO in case of formate ionic liquids) was added. The complete content of the reactor was added to this cylinder, the reactor washed with acetone (or with MeOH in case of formate ionic liquids) (3×2 mL) and the washing also added to the cylinder. After mixing, 0.5 mL of this solution was analysed by ¹H-NMR with as little delay as possible (maximum 90 minutes), as decomposition of formic acid becomes favoured after depressurisation. In the case formate ionic liquids were used, the relative growth of the formyl integral in the ¹H-NMR spectrum compared to the spectrum before the reaction was quantified using 1,4-dioxane as internal standard again.

7) Continuous-flow experiments

The equipment used for all continuous-flow experiments has been described in detail elsewhere.⁴ The setup was not placed inside an incubator and a very similar window-equipped steel autoclave ($V = 10$ mL) as used for batch catalyses served as continuous stirred tank reactor (CSTR).

Continuous-flow CO₂ hydrogenation

The catalyst solution was prepared in the same way as described for batch catalysis, transferred to the argon filled reactor via syringe, and the reactor closed and sealed with two ball valves at the inlet and the outlet.

The sealed reactor was inserted into the reaction rig, heated to 50 °C, and the bypass opened. All lines were thoroughly purged with CO₂ flow at 200 bar with 150 mL_N/min for at least 1 hour. Thereafter, the ball valve at the inlet of the autoclave was carefully opened, and the reactor pressurised to 200 bar. Then the inlet of the autoclave was sealed again and the dosage of H₂ was started with 20 mL_N/min. For starting the reaction, the reactor bypass was closed and the inlet and the outlet of the autoclave were opened to allow the flow to pass through the stirred liquid phase in the reactor. Extracts were collected by passing the exiting stream through a cooling trap filled with water (ca. 6 mL) and glass beads, cooled with ice-water. Cooling traps were periodically changed and analysed for formic acid, formic acid/amine adducts and IL content by ¹H-NMR (typically with 256 scans to enhance the signal to noise ratio). Analysis procedure was the same as described for batch catalysis.

For stopping the continuous reaction or extraction, the ball valves at the reactor were sealed, the reactor bypass opened, and a depressurisation ramp (3 bar/min) was applied. After complete depressurisation to 1 atm, the reactor was dismantled, cooled to 0 °C, carefully vented, and the content analysed as described for batch catalysis. After every continuous experiment the setup was cleaned by purging with MeOH (10 mL/min) for at least 1 hour and extracting with CO₂ (200 mL_N/min, 120 bar) overnight. Representative ¹H-NMR spectra of samples from the continuous-flow CO₂ hydrogenation experiments are depicted in Figures 2 and 3.

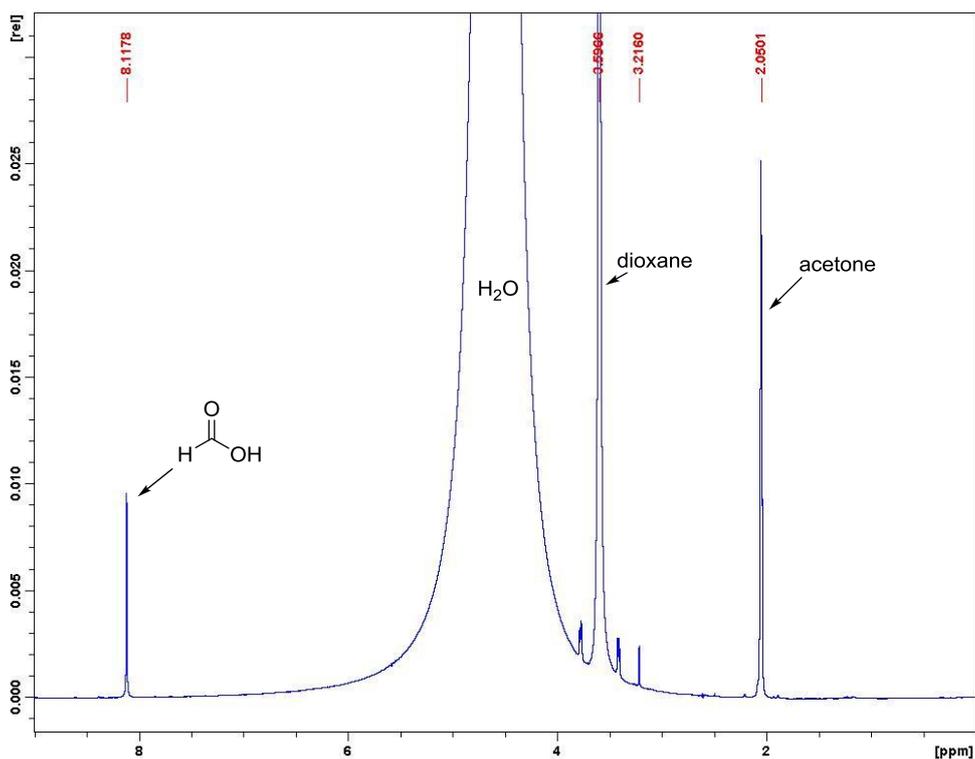


Figure 2. ^1H -NMR spectrum of the cooling trap content collected after 42 h from the continuous-flow CO_2 hydrogenation using catalyst **4** in non-volatile base **5** with 1,4-dioxane as internal standard. The small signal at 3.2 ppm originates from residual MeOH from cleaning the reaction rig.

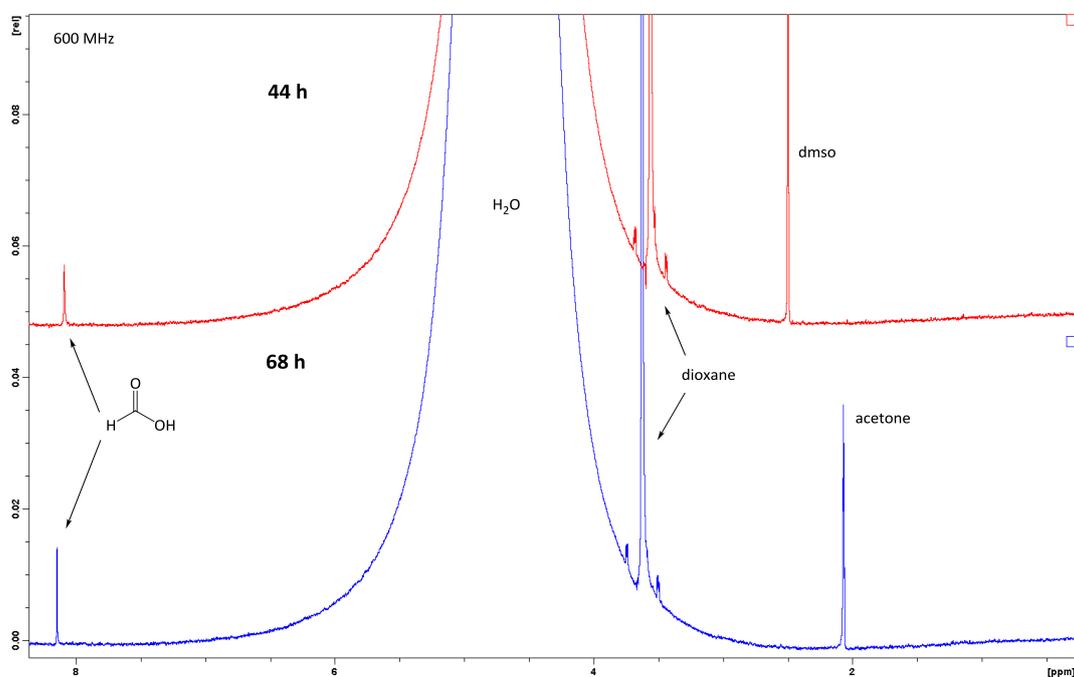


Figure 3. ^1H -NMR spectra of cooling trap contents collected after 44 h and 68 h from continuous-flow CO_2 hydrogenation using catalyst **4** in QuadraPureTM-DMA/IL **11** with 1,4-dioxane as internal standard.

Figure 4 b) shows the $^1\text{H-NMR}$ spectrum of the amine-functionalised IL **5** after use in continuous-flow reaction for 211 hours. The spectrum is virtually unchanged compared to the spectrum showed in Figure 4 a) which depicts the unused IL **5**, indicating a reasonable IL stability under reaction conditions.

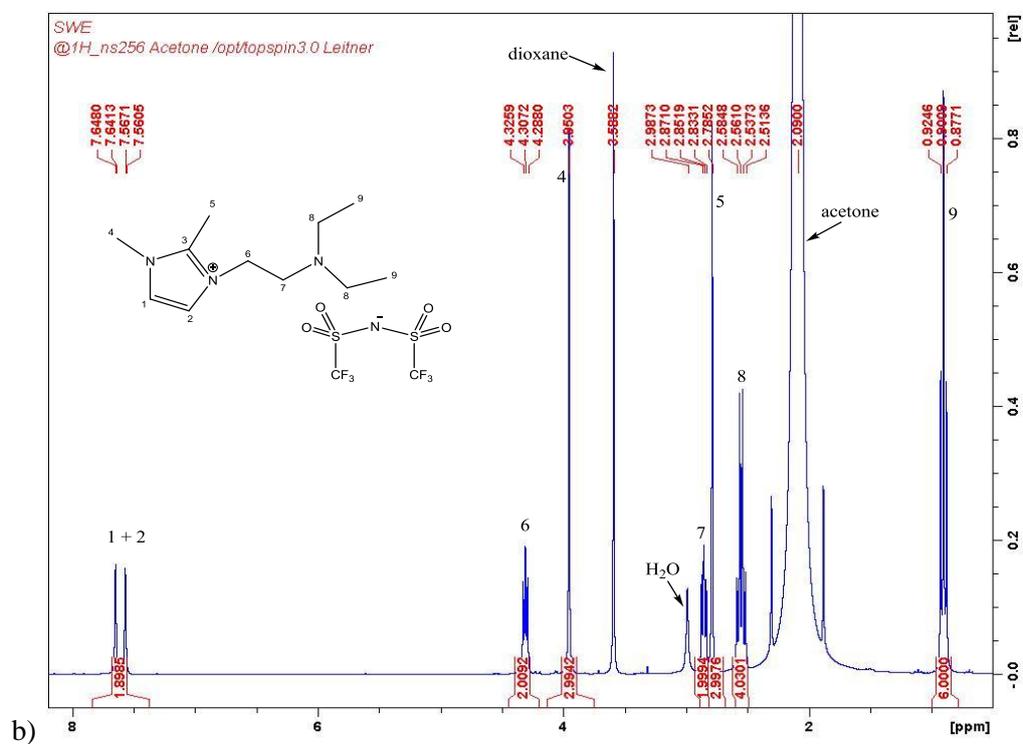
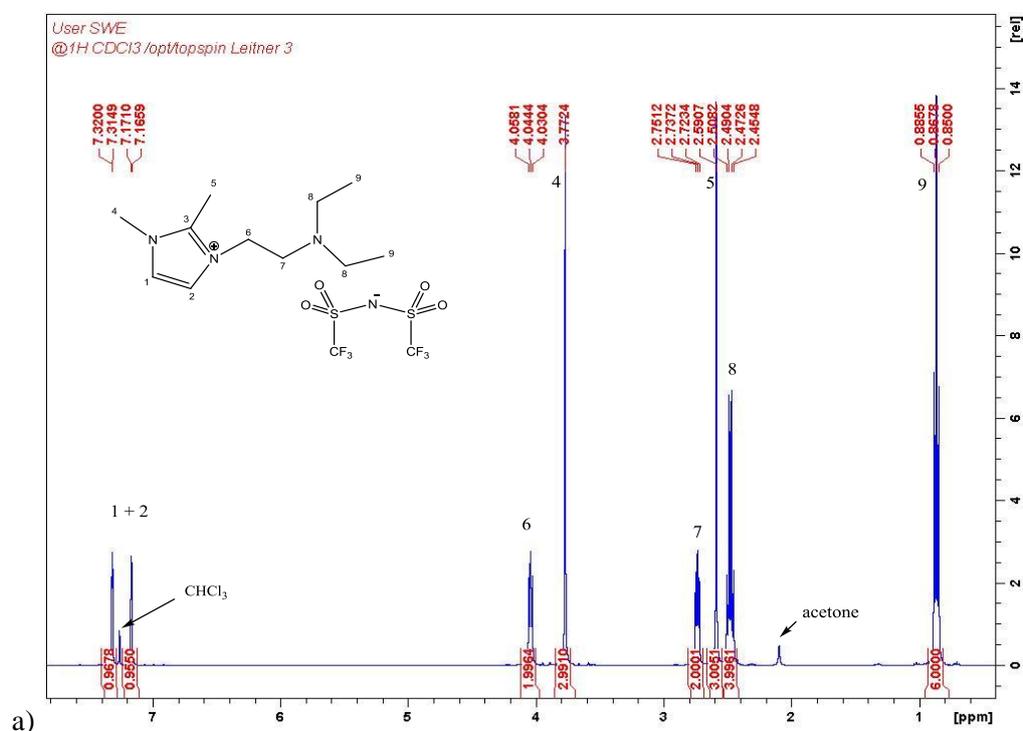


Figure 4. $^1\text{H-NMR}$ spectra of the amine-functionalised IL **5**. a): Unused IL **5**. b) IL **5** after use in continuous-flow reaction for 211 hours; huge acetone signal due to IL recovery from reactor with acetone; water signal due to use of wet acetone. The integral of protons 1 and 2 appear a little bit small in both cases, which is due to their longer relaxation times in NMR.

Continuous-flow HCO₂H extraction from non-volatile bases

The desired amount of formic acid was transferred to the autoclave via syringe, and the exact mass was determined by weighing the syringe before and after the addition. The basic ionic liquid (typically 1.0 mL) was added in the same way. After sealing the autoclave, the solution was stirred for at least 10 minutes with the magnetic stir bar. In the case QuadraPure™-DMA was used as base, 0.5 g of the resin were weighed into the reactor prior to the addition of formic acid and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (1.0 mL).

The continuous-flow experiment and the analysis of cooling trap contents was performed as described for the continuous-flow CO₂ hydrogenation. Representative ¹H-NMR spectra of continuous-flow extraction experiments are depicted in Figures 5-7.

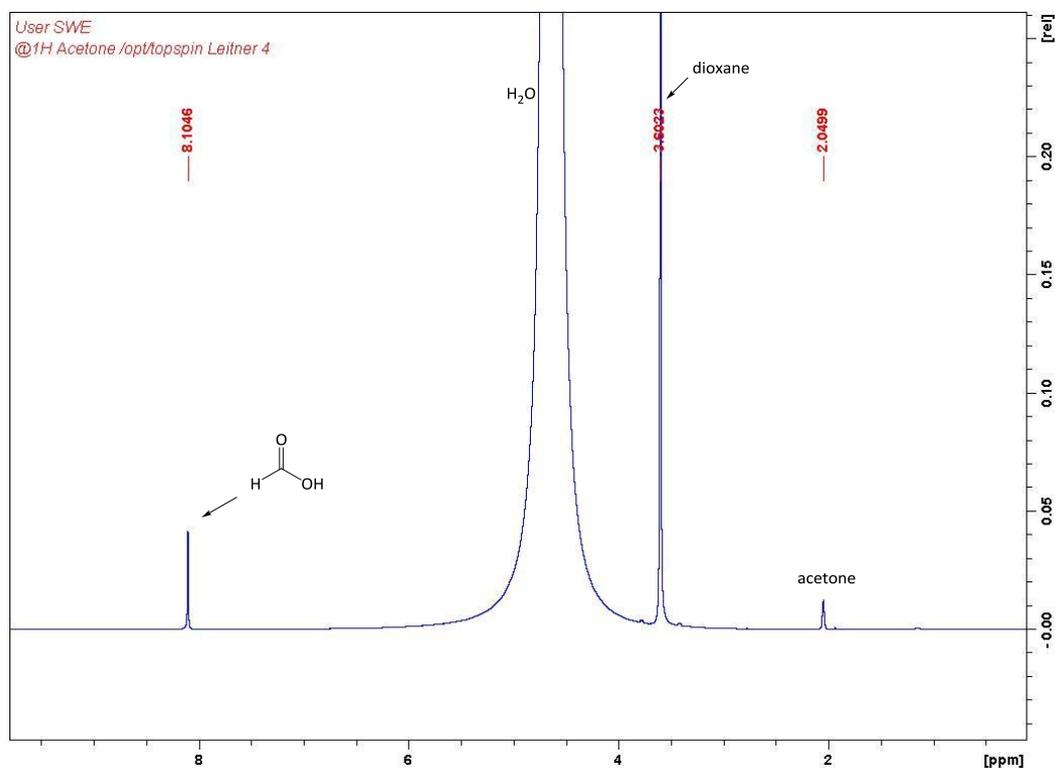


Figure 5. ¹H-NMR spectrum of the cooling trap content collected after 22 h from the continuous-flow HCO₂H extraction from non-volatile base **5** with 1,4-dioxane as internal standard.

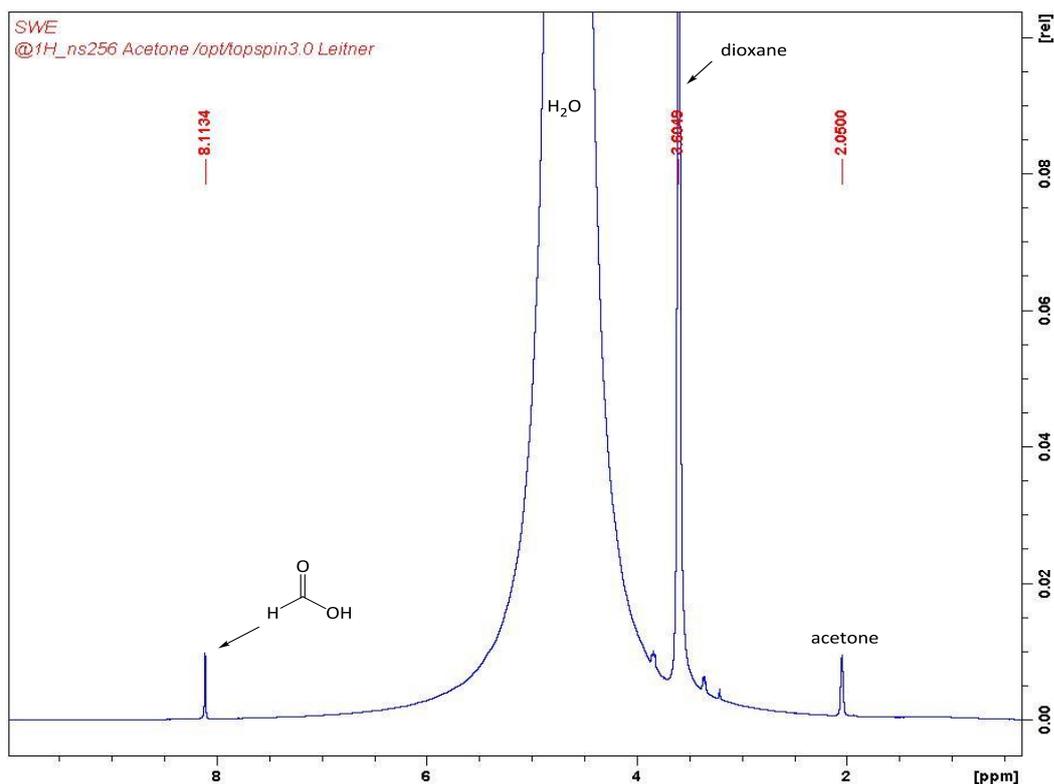


Figure 6. ¹H-NMR spectrum of the cooling trap content collected after 115 h from the continuous-flow HCO₂H extraction from QuadraPure™-DMA/IL **11** with 1,4-dioxane as internal standard. The small signal at 3.2 ppm relates to MeOH impurities from cleaning the reaction rig.

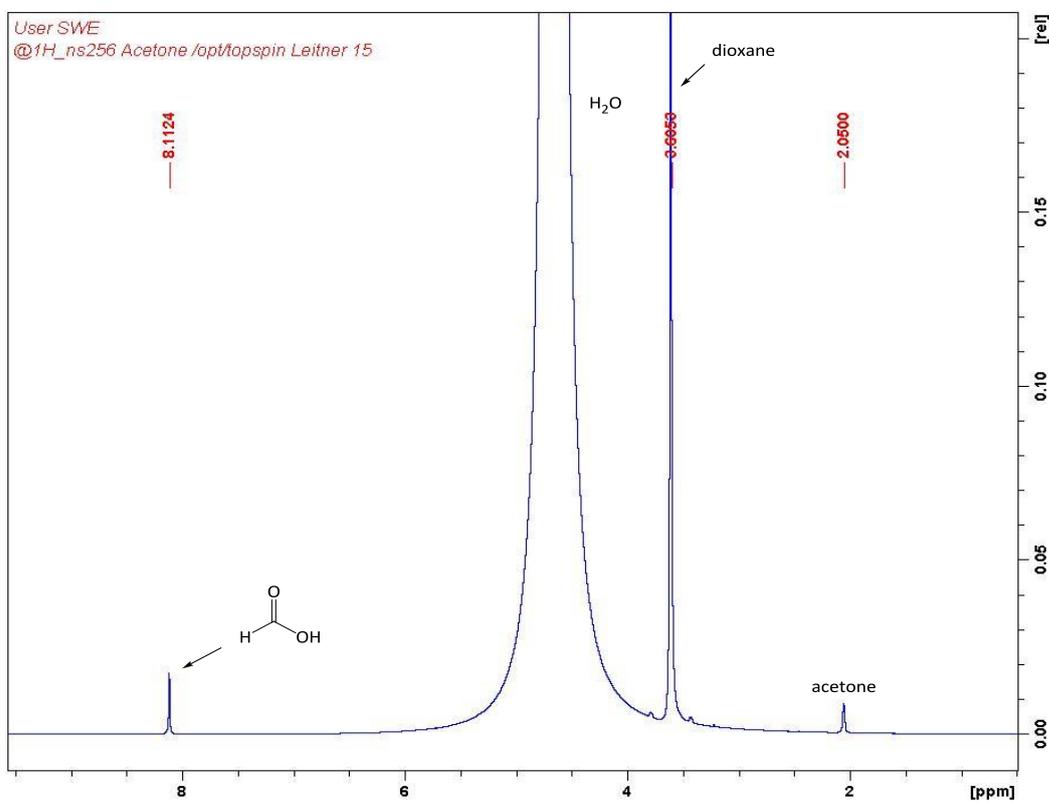


Figure 7. ¹H-NMR spectrum of the cooling trap content collected after 43 h from the continuous-flow HCO₂H extraction from non-volatile base **10** with 1,4-dioxane as internal standard.

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