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Continuous-Flow Hydrogenation of Carbon Dioxide to Pure Formic Acid using an Integrated $scCO_2$ Process with Immobilized Catalyst and Base**

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Dedicated to Professor David J. Cole-Hamilton

The use of carbon dioxide as carbon resource provides an attractive option in the increasing efforts to reduce the carbon footprint at the interface between the energy and the chemical sector.[1] The hydrogenation of CO_2 to formic acid (HCO_2H) has been studied intensively in this context.[2] This transformation offers direct access to chemical products based on waste material from the energetic use of fossil fuels, opens a possible route to convert CO_2 into CO, and is discussed as a potential option for hydrogen storage. Homogeneous catalysts for the addition of hydrogen to CO_2 have been developed since the mid-seventies, and remarkable progress in terms of catalyst activity has been achieved.[2] However, all currently known systems produce salts, adducts, or derivatives of formic acid because the formation of pure formic acid from CO_2 and H_2 is strongly disfavored by entropy shifting the equilibrium far to the left (Scheme 1).[2a,c] Thus, multistep downstream processes are required for removal of the primary products from the catalyst to avoid back-reaction, and their subsequent cleavage to obtain pure formic acid.[3,4] Integration of molecular catalyst development with new reaction engineering concepts is needed to address this limitation of CO_2 hydrogenation, because free HCO_2H is eventually required for most applications.

$$CO_2(g) + H_2(g) \rightleftharpoons HCO_2H(l)$$
$$\Delta G^\circ = 32.8\ \mathrm{kJ\,mol^{-1}} \quad \Delta H^\circ = -31.5\ \mathrm{kJ\,mol^{-1}} \quad \Delta S^\circ = -216\ \mathrm{kJ\,mol^{-1}}$$

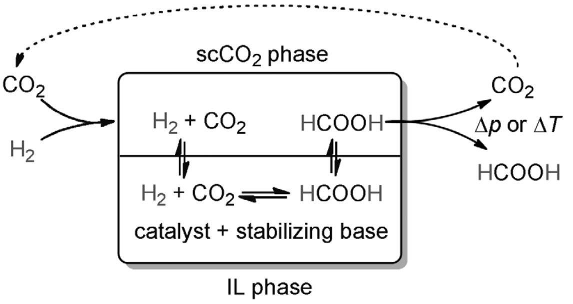
$$CO_2(g) + H_2(g) + NH_3(aq) \rightleftharpoons HCO_2^-(aq) + NH_4^+(aq)$$
$$\Delta G^\circ = -9.5\ \mathrm{kJ\,mol^{-1}} \quad \Delta H^\circ = -84.3\ \mathrm{kJ\,mol^{-1}} \quad \Delta S^\circ = -250\ \mathrm{kJ\,mol^{-1}}$$

Scheme 1. Thermodynamics of CO_2 hydrogenation to formic acid in the absence and presence of base.[2c]

Early patents by BP and some recent studies describe multistep processes where the initially formed azeotropic adduct of HCO_2H and NEt_3 is transformed into a thermally cleavable salt by exchange of the base.[3] Multiphasic reaction systems have also been investigated to separate the adduct from the catalyst, but these still necessitate downstream purification.[4] BASF recently presented a new process using $NHex_3$ as product-stabilizing base with a ruthenium catalyst in protic media.[4b,d] The resulting $HCO_2H/NHex_3$ adduct can be separated and cleaved into free formic acid and amine by distillation. Zhang et al. proposed a process in which an immobilized ruthenium catalyst was used in water together with an ionic liquid (IL) containing a tertiary amino group as nonvolatile base.[5] After reaction, the solid catalyst is separated by filtration, and the formic acid can be distilled out from the basic IL. Yasaka et al. proposed the use of imidazolium-based ILs with formate anions to stabilize HCO_2H.[6]

Herein we present a new concept that allows the continuous-flow hydrogenation of supercritical CO_2 ($scCO_2$) with integrated product separation from an immobilized catalyst and stabilizing base to produce pure HCO_2H in a single processing unit.[7]

The concept is based on a biphasic reaction system consisting of $scCO_2$ as mobile phase and an IL as stationary phase[8] containing the catalyst and a nonvolatile base



Scheme 2. Process for the direct continuous-flow hydrogenation of CO_2 to free formic acid based on a two-phase system with $scCO_2$ as extractive mobile phase and an ionic liquid (IL) as stationary phase containing the catalyst and the stabilizing base.

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(Scheme 2). The use of $scCO_2$ as both reactant and extractive phase affords continuous removal of product from the reactor, thereby causing the reaction equilibrium to readjust in the reactive phase. Facile recovery of pure HCO_2H can then be achieved by simple decompression of the CO_2 flow downstream.[9] The negligible vapor pressure of the components in the IL phase renders them virtually insoluble in $scCO_2$,[9] and pure HCO_2H that is free of any cross-contamination can be obtained without interrupting the working catalyst inside the reactor.

First we identified suitable combinations of transition metal catalysts and ionic liquid matrices in batch experiments, starting with the standard IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM NTf_2) and NEt_3 as base for the stabilization of HCO_2H under 100 bar total pressure of H_2/CO_2 (1:1) at a reaction temperature of $T = 50\,°C$ (see the Supporting Information). The precursor complexes were combined with monosulfonated triphenylphosphine (TPPMS) in metal-to-ligand ratios of between 1:3 and 1:3.5. The sodium cation of TPPMS was exchanged for tetrabutylphosphonium (PBu_4) or 1-ethyl-3-methylimidazolium (EMIM) counterions to match the solvent properties of the IL.[8] Selected results are summarized in Table 1.

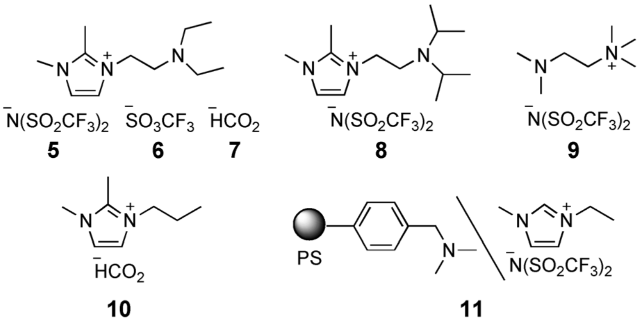
Table 1: Catalyst optimization for use in ILs with NEt_3.[a]

Entry	Cat. no.	Precursor	Ligand	Additive (equiv)	t [h]	TON[b]	TOF[c] [h^{-1}]	Formic acid/ amine[d]
1	**1**	[Rh(cod)acac]	EMIM TPPMS	–	2	52	26	0.05
2	**2**	$[Ru(cod)Cl_2]_n$	PBu_4TPPMS	–	0.5	425	850	0.43
3	**2**	$[Ru(cod)Cl_2]_n$	PBu_4TPPMS	–	16	850	43	0.85
4	**3**	$[Ru(cod)(methallyl)_2]$	PBu_4TPPMS	–	0.5	314	627	0.34
5	**3**	$[Ru(cod)(methallyl)_2]$	PBu_4TPPMS	–	16	1003	63	1.00
6	**4**	$[Ru(cod)(methallyl)_2]$	PBu_4TPPMS	EMIM Cl (2)	0.5	516	1032	0.52
7	**5**	$[Ru(cod)(methallyl)_2]$	PBu_4TPPMS	EMIM Cl (10)	0.5	545	1089	0.55

[a] Conditions: $T = 50\,°C$, $p(H_2) = p(CO_2) = 50$ bar, $V(IL) = 2.89$ mL, $V(NEt_3) = 1.11$ mL, V(autoclave) = 12–13 mL, c(cat.) = 2 μmol mL^{-1}; [b] TON = mol(HCO_2H) per mol(cat.); [c] TOF = TON h^{-1}; [d] mol(HCO_2H) per mol(amine) after 20 h.

The ruthenium-based in situ catalyst systems $[\{Ru(cod)Cl_2\}_n]/PBu_4TPPMS$ (1:3 molar ratio; **2**) and $[Ru(cod)(methallyl)_2]/PBu_4TPPMS$ (1:3.5; **3**) showed much higher activities than the Rh-based [Rh(cod)acac]/EMIM TPPMS (1:3) system **1** (Table 1, entries 1–5). With catalyst **3**, the amount of formic acid formed after 16 h corresponded to a HCO_2H/NEt_3 ratio of 1:1 (Table 1, entry 5). Superior activity in terms of turnover frequency (TOF) was obtained with the chloride-containing precursor in system **2** as compared to **3** (Table 1, entries 2 and 4). The deliberate addition of chloride (2 equiv of EMIM Cl per Ru) to the catalyst system **3** also improved the TOF by more than 50% from 627 h^{-1} to 1032 h^{-1} (Table 1, entries 4 and 6). Larger amounts of chloride did not afford significant improvement (Table 1, entry 7). The activity of this IL-adjusted system **4** compares well with those of similar Ru/PAr_3 catalysts in organic solvents or water.[2] It thus provides a suitable basis for further process development and was used in all of the following experiments.

We then focused on the integration of a nonvolatile base for intermittent product stabilization. Following previous developments,[5,6] we synthesized a set of $scCO_2$-insoluble organic salts containing amine functionalities (**5**–**9**) or intrinsic anion basicity (**10**) to stabilize HCO_2H (Scheme 3; see the Supporting Information). Only compounds **5** and **9** were room-temperature ILs, but **8** and **10** liquefied under reaction conditions. **6** and **7** had to be used as 1:1 molar mixtures with the low-melting salt **5**.



Scheme 3. Nonvolatile bases tested as stationary phases for CO_2 hydrogenation using catalyst **4** (PS = polystyrene).

Catalyst system **4** led to formation of HCO_2H under standard conditions ($p(CO_2) = p(H_2) = 50$ bar, $T = 50\,°C$) in all of the basic IL phases without additional NEt_3 (Table 2). Among the amine-functionalized cations, the imidazolium-based structures **5**–**7** gave the highest formic acid concentrations (Table 2, entries 1–3). Variation of

Table 2: Evaluation of nonvolatile bases as stationary phases for CO_2 hydrogenation using catalyst **4**.[a]

Entry	Nonvolatile base	TON[b]	TOF_{ini}[c] [h^{-1}]	Formic acid/ amine[d]
1	**5**	73	>23	0.05
2	**8**	25	>8	0.02
3	**9**	27	>12	0.03
4	**5**/**6**[e]	126	>36	0.10
5	**5**/**7**[e]	599	>314	0.54
6	**10**	1968	>295[f]	–
7	**11**[g]	583	>234	0.47[h]

[a] Conditions: $T = 50\,°C$, $p(H_2) = p(CO_2) = 50$ bar, V(nonvolatile base) = 1.0 mL, V(autoclave) = 12–13 mL, c(cat.) = 2 μmol mL^{-1}; [b] TON = mol(HCO_2H) per mol(cat.) after 20 h reaction time; [c] TOF = TON h^{-1} after 2 h reaction time; [d] mol(HCO_2H) per mol(amine) after 20 h; [e] 1:1 molar ratio; [f] after 1 h reaction time; [g] 0.5 g basic resin in 1.0 mL EMIM NTf_2; [h] calculated for a theoretical amine capacity of the resin of 5 mmol g^{-1}.

the anions revealed a consistent increase in TONs and TOFs following the order $NTf_2^- < OTf^- < HCO_2^-$ that parallel their increasing basicities, dielectric constants, and Kamlet–Taft parameters β (Table 2, entries 1, 4, and 5).[10] Using the amine-free IL **10** with a formate anion also resulted in high TONs and TOFs (Table 2, entry 6). Notably, the TOF of 314 h^{-1} obtained in the 1:1 molar mixture of ILs **5** and **7** is one order of magnitude higher than the highest activity previously reported in ILs without addition of nonionic amines. The high formic acid-to-amine ratios of up to 1:2 indicate that high HCO_2H loadings can be achieved in these media, a beneficial property for potential extraction processes.

Immobilizing the stabilizing base on the surface of a solid support was also shown to be effective for the first time. A polystyrene resin functionalized with diethylamine groups (QuadraPure-DMA, Johnson Matthey) suspended in non-functionalized EMIM NTf_2 (**11**) gave high initial TOFs above 200 h^{-1}, together with a high formic acid-to-amine ratio of approximately 1:2.

The extraction of free HCO_2H from these nonvolatile bases with $scCO_2$ was assessed in a custom-built continuous-flow setup with precise control over pressure, temperature, and flow.[11] The solubility of HCO_2H in $scCO_2$ was determined to be at least 49 $g\,L^{-1}$ at 50 °C and 100 bar. Figure 1 shows selected examples for the extraction efficiency (mass of extracted HCO_2H/mass of initially added HCO_2H) over time at initial formic acid-to-base ratios between 1.1–1.3 and comparable $scCO_2/H_2$ flow values (see the Supporting Information for details). Extraction from the formate IL **10** was sluggish, reaching an extraction efficiency of only 14 % after 74 h at an average rate of 0.9 $mg\,h^{-1}$. Increasing the temperature from 50 °C to 70 °C did not significantly improve the extraction rate. HCO_2H extraction from the IL-suspended resin QuadraPure-DMA **11** gave an extraction efficiency of 24 % after 91 h at an average rate of 0.4 $mg\,h^{-1}$. Recovery of HCO_2H from the amine-functionalized IL **5** proceeded more effectively, and after 95 h an extraction efficiency of 84 % was obtained, corresponding to initial extraction rates of at least 3.5 $mg\,h^{-1}$. Up to 94 % mass recovery was reached after longer times. Pure HCO_2H without any cross-contamination was extracted with $scCO_2$ from all of the bases according to ^1H NMR spectroscopic analysis of the extracts.

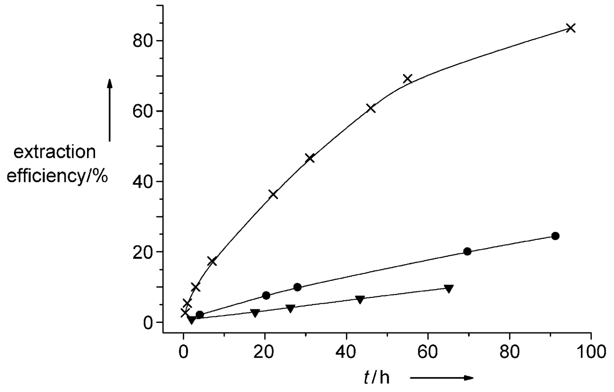


Figure 1. Extraction efficiency (mass of extracted HCO_2H/mass of initially added HCO_2H) during extractions of HCO_2H with $scCO_2$ from immobilized bases. Lines are only provided as a guide for the eye. Conditions: $T = 50$ °C, $p = 200$ bar, $V(IL) = 1.0$ mL, $V(CO_2) = 200$ $mL_N\,min^{-1}$, $V(H_2) = 20$ $mL_N\,min^{-1}$, $V(autoclave) = 10$ mL; **5** (×): $m(HCO_2H) = 159$ mg, acid/amine = 1.2; **10** (▼): $m(HCO_2H) = 375$ mg, acid/formate = 1.3, after 26 h $T = 70$ °C; **11** (●): $m(resin) = 0.5$ g, $m(HCO_2H) = 130$ mg, acid/amine = 1.1 calculated for a theoretical amine capacity of the resin of 5 $mmol\,g^{-1}$.

Based on these data, the IL-adjusted catalyst system **4** was combined with selected nonvolatile bases as the stationary phase for the continuous-flow CO_2 hydrogenation process with integrated product extraction. A high-pressure steel autoclave ($V = 10$ mL) equipped with a window was charged with a solution of catalyst **4** in the amine-functionalized IL **5** ($V = 1.0$ mL, $c(cat.) = 2$ $\mu mol\,ml^{-1}$), heated to 50 °C and pressurized to 200 bar with CO_2. The continuous reaction was started by passing the supercritical CO_2/H_2 flow ($V(CO_2) = 200$ $mL_N\,min^{-1}$, $V(H_2) = 20$ $mL_N\,min^{-1}$) through the reactor under vigorous stirring. Extracts were collected by passing the exiting stream through cooling traps filled with water, which were periodically changed and analyzed by ^1H NMR. The error in the determination of the HCO_2H concentration was determined to be in the range 2–10 % by calibration measurements (see the Supporting Information). Already in the first sample after 5 h, a HCO_2H concentration corresponding to a TON of 28 was detected. The cumulative TONs over time are depicted in Figure 2. The TON of HCO_2H produced after 211 h was 358. Pronounced catalyst deactivation was observed after 70 h in this experiment, which could also be visually followed by color changes from bright yellow to orange. The ^1H NMR spectrum of IL **5** recovered from the reactor after 211 h on-stream was virtually unchanged (see the Supporting Information), indicating a reasonable stability of the IL under sustained reaction conditions.

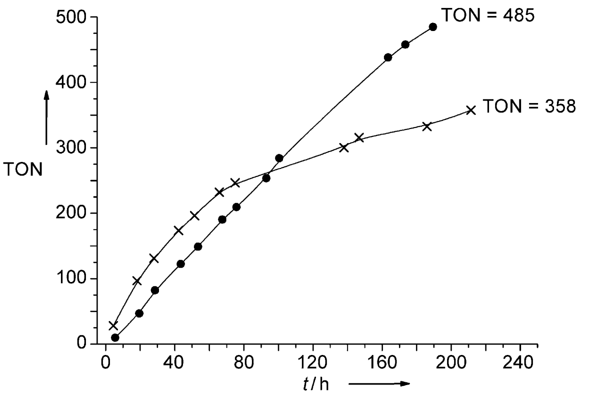


Figure 2. Cumulative turnover numbers for catalyst **4** in IL **5** (×) and in QuadraPure-DMA/IL (**11**, ●) with respect to time. Lines are only provided as a guide for the eye. Conditions: $T = 50$ °C, $p = 200$ bar, $V(IL) = 1.0$ mL, $V(CO_2) = 200$ $mL_N\,min^{-1}$, $V(H_2) = 20$ $mL_N\,min^{-1}$, $V(autoclave) = 10$ mL, $c(cat.) = 2$ $\mu mol\,mL^{-1}$.

When the reactor was charged with a solution of catalyst **4** in EMIM NTf_2 ($V = 1.0$ mL, $c(cat.) = 2$ $\mu mol\,mL^{-1}$) with QuadraPure-DMA **11** (0.5 g) suspended therein, the continuous reaction conducted under the same conditions showed a slightly slower initial rate, but reached higher TONs of 485 after 190 h. As judged from the more constant slope of the TON curve, catalyst stability was significantly higher with the heterogeneous QuadraPure-DMA base, and the initial activity was largely retained even after 200 h time on-stream. ^{1}H NMR analysis of the extracts confirmed that pure HCO_2H was extracted in both cases, and no components of the stabilizing medium were entrained (see the Supporting Information). Thus, separation and continuous removal of pure HCO_2H with $scCO_2$ flow was effectively realized.

In summary, we have successfully demonstrated a new process that allows the continuous hydrogenation of CO_2 to pure formic acid in a single process unit. This was achieved through an integrated design and development of the macroscale process, the mesoscale separation strategy, and the molecular-scale catalyst system. Careful adjustment of all components of the stationary phase led to systems with high activities (initial TOFs $> 314\ h^{-1}$) matching or even surpassing the performance of similar ruthenium catalysts in conventional solvents. Together with the high formic acid loadings achieved under equilibrium conditions, these data indicate that the rates of formic acid extraction are currently the limiting factor under continuous-flow conditions. Therefore, the key design parameter for future optimization of this approach appears to be the development of matrices that combine a sufficient stabilizing effect for formic acid during formation with a favorable partitioning of HCO_2H into the $scCO_2$ phase.

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