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Homogeneous hydrogenation of saturated bicarbonate slurry to formates using multiphase catalysis†

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Formic acid and formate salts are key intermediates along the pathways for CO₂ utilization and hydrogen storage. Herein we report a highly efficient multiphase catalytic system utilizing a ruthenium PNP pincer catalyst for converting supersaturated bicarbonate solutions and slurries to aqueous formate solutions up to 12 M in molarity. The biphasic catalytic system delivers turnover frequencies up to 73 000 h⁻¹ and remains stable for up to 474 000 turnovers once reaction conditions are optimized.

Current CO₂ emissions are a concern regarding climate change.^{1,2} Consequently, efforts have been made to capture CO₂ efficiently from the atmosphere and to utilize it for various goals.³ Among the various CO₂ utilization strategies, its chemical conversion to C₁ building blocks has been the focus of intense research effort over the last decades.^{4–6} The common utilization routes rely on CO₂ reduction that can be performed electrochemically^{7,8} or utilize molecular hydrogen as the reducing agent.^{9,10} The latter can be further split into heterogeneous processes that mainly target methanol as a main product and homogeneous reduction protocols that typically produce formic acid and its salts.^{11–27} Although in recent years there have been significant progress in base metal catalysts for CO₂ hydrogenation, namely iron,^{28–32} cobalt^{33–37} and manganese,^{38–40} the state-of-the-art in homogeneous CO₂ hydrogenation is dominated by noble metal catalysts. Fig. 1 depicts several representative examples of such complexes. One of the first highly active CO₂ hydrogenation catalysts reported by Nozaki and co-workers²⁷ (2, Fig. 1) shows exceptional turnover frequencies (TOFs) up to 150 000 h⁻¹ in hydrogenating CO₂ in the presence of aqueous KOH/THF mixtures at 120–200 °C. A family of iridium catalysts reported by Himeda and co-workers^{11,12,16,17,41,42} with complex 3 (Fig. 1) as a representative example were also noted for their CO₂ hydro-

genation activity pronounced in aqueous solutions at room temperature and 1 bar of hydrogen pressure. Importantly, operation of these complexes could be switched between CO₂ hydrogenation and formic acid dehydrogenation by controlling the pH of the reaction solution. Finally, our group reported a highly active ruthenium catalyst (1, Fig. 1), which was active for both CO₂ hydrogenation and formate dehydrogenation albeit in organic solvents in the presence of organic bases.

From the process standpoint, homogeneous CO₂ hydrogenation should fulfil several requirements to be practical. Firstly, the catalyst should be sufficiently stable to provide high, economically relevant productivity. Secondly, the catalyst should be separable from the formate product that can easily be dehydrogenated once the hydrogenation reactor is decompressed. The latter has recently been addressed by immobilizing homogeneous catalysts on solid supports⁴³ and encapsulating them into porous carriers.^{44,45}

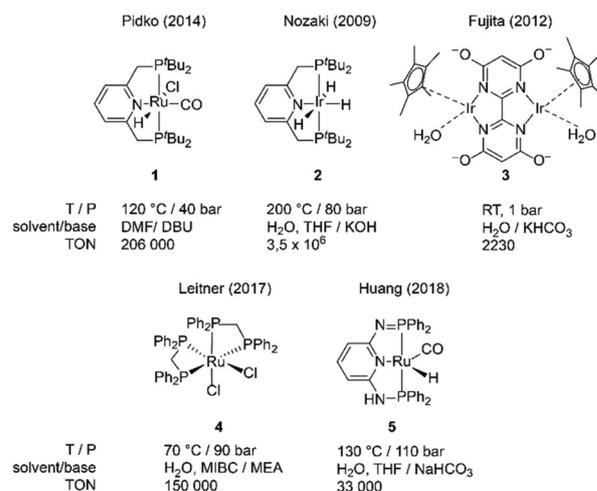


Fig. 1 Representative homogeneous catalysts for the hydrogenation of CO₂ to formates (1–3) and examples of catalysts operating in biphasic systems (4, 5), allowing for easy product separation.

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While this approach greatly simplifies catalyst separation, it has a drawback of consistently lower activity of the immobilized catalyst compared to its free molecular predecessor.

An approach alternative to immobilization makes use of biphasic solvent systems,^{46,47} in which the catalyst and reactants reside in different phases. Formate salts typically reside in the aqueous phase while the organometallic catalyst species remain in the organic phase and the catalyst and product(s) separation in the biphasic system can be done by simple decantation. Successful utilization of biphasic catalyst systems for CO₂ hydrogenation has been demonstrated with catalysts **4**⁴⁶ and **5**⁴⁷ shown above and the development of highly active biphasic CO₂ hydrogenation is our primary goal in this work.

Herein we report the development of a highly active multi-phase catalyst system based on our Ru-PNP catalyst **1** enabling the hydrogenation of supersaturated aqueous bicarbonate to formate with outstanding efficiency. While complex **1** is a highly competent catalyst in fully organic media, *e.g.* DMF/DBU system utilized in earlier studies¹³ it performed poorly in aqueous environments. Our initial trials using **1** at 40 bar of equimolar H₂/CO₂ in water in the presence of KOH base provided very low formate yields (Table 1, entries 3 and 6) with a maximal TON of 1573 at 90 °C. Assuming the low solubility of **1** to be the major factor limiting catalytic performance in the aqueous media, we performed CO₂ hydrogenation tests in the presence of an additional organic solvent. Both water-miscible DMF and immiscible toluene addition could improve the formate yields (Table 1); however, the KOH conversion remained limited to a maximum of 26%. We envisioned that such limitation might stem from the poor transport of ionic species across the phase boundary and employed a phase-transfer catalyst (PTC, methyltrioctylammonium chloride) to enhance it. Our choice of PTC was methyltrioctylammonium chloride which combines several features critical for practical applications – its wide commercial availability, low price and high affinity for organic solvents that prevents the loss of PTC to the aqueous phase. The latter is a main drawback of some alternative PTCs, *e.g.* tetrabutylammonium salts, that are water soluble and can additionally contaminate the resulting formate product. Addition of PTC resulted in a significant increase of formate yields in biphasic catalytic systems (Table 2).

Table 1 Solvent effect on the hydrogenation of CO₂ with KOH as the base^a

Entry	Solvent	KOH (mmol)	TON	Yield (%)
1	H ₂ O/DMF	2.5	5627	26
2	H ₂ O/toluene	2.5	3125	13
3	H ₂ O	2.5	745	3.3
4	H ₂ O/DMF	5.0	7610	18
5	H ₂ O/toluene	5.0	2992	7.5
6	H ₂ O	5.0	1573	3.7

^a Reaction conditions: 2 mL of total solvent (1/1 in the case of mixed solvent systems), 0.107 μmol catalyst **1**, *T* = 90 °C, *p* = 40 bar (*p*_{H₂} = *p*_{CO₂} = 20 bar), *t* = 3 h.

Table 2 Effect of using methyltrioctylammonium chloride as the phase-transfer catalyst in the hydrogenation of CO₂ in a biphasic system, using KOH as a base^a

Entry	PTC (mmol)	KOH (mmol)	TON	Yield (%)
1	No	2.5	3125	13
2	No	5.0	2992	7.5
3	0.025	5.0	20 060	52
4	0.29	5.0	17 732	46
5	0.052	14	16 509	14

^a Reaction conditions: 2 mL of total solvent (H₂O/toluene = 1/1), 0.107 μmol catalyst **1**, *T* = 90 °C, *p* = 40 bar (*p*_{H₂} = *p*_{CO₂} = 20 bar), PTC is methyltrioctylammonium chloride, *t* = 3 h.

In the same screening experiment we noted that elevated base concentrations consistently resulted in lower formate yields, implying the limited stability of **1** in a highly alkaline medium (Table 2). Circumventing this, we opted to perform the direct hydrogenation of bicarbonates – a process with additional advantage of using hydrogen as the only gaseous feedstock. Similar to the H₂O/KOH system, the hydrogenation of H₂O/KHCO₃ shows a limited efficiency in pure water or in the absence of a PTC (Table 3). However, a biphasic medium with PTC provides excellent TON values >100 000 with yields significantly higher than those obtained with potassium hydroxide base (Table 3). In addition, this catalytic systems retains its composition after catalysis with negligible extent of Ru leaching into the aqueous phase as evidenced by ICP-MS analysis of the spent product mixtures (see the ESI†). While the water-toluene biphasic medium provided good catalytic performance, catalysis can readily be performed using other organic solvents that have higher affinity to water compared to toluene. For example, ethereal solvents, 1,4-dioxane and THF were found to form a biphasic mixture in the presence of a high formate salt content with THF-water medium providing a performance similar to that of toluene (see Table 3 and S16, 17 of the ESI† for details).

In sharp contrast with hydroxide bases, a gradual increase of KHCO₃ loading leads to the marked increase in both observed TON and final formate yield. For example, we could

Table 3 Hydrogenation of potassium bicarbonate, with and without using a phase-transfer catalyst^a

Entry	Solvent	PTC (mmol)	KHCO ₃ (mmol)	TON	Yield (%)
1	H ₂ O	No	10	3963	4.5
2	H ₂ O/toluene	No	10	4263	4.8
3	H ₂ O/toluene	0.055	10	66 495	78
4	Toluene	0.055	5.0	289	0.6
5	H ₂ O/toluene	0.055	5.0	26 897	65
6	H ₂ O/toluene	0.055	14	102 593	86
7	H ₂ O/THF	0.055	5.0	29 923	71
8	H ₂ O/dioxane	0.055	5.0	6096	14

^a Reaction conditions: 2 mL of total solvent (1/1 in the case of mixed solvent systems), 0.107 μmol catalyst **1**, *T* = 90 °C, *p* = 40 bar (*p*_{H₂} = 40 bar), *t* = 3 h, PTC = methyltrioctylammonium chloride.



utilize KHCO_3 loadings of up to $14 \text{ mmol mL}_{\text{H}_2\text{O}}^{-1}$ and obtain final yields in the extent of 86% corresponding to a TON of 102593 (Table 3, entry 6). Remarkably, even at the temperature of 90°C , the reaction mixture is saturated in potassium bicarbonate with the main fraction of KHCO_3 remaining solid. In line with the solubility of potassium formate being significantly higher than that of bicarbonate our approach effectively transforms bicarbonate slurries to $>50\%_{\text{wt}}$ formate solutions with no need for product concentration.

The trend of increasing formate yield as a function of initial bicarbonate loading was confirmed in a separate study depicted in Fig. 2. Upon the increase of KHCO_3 loading from 2 to 14 mol per litre water, the formate yield increased from 63 to 86%. Interestingly, the catalytic reaction apparently accelerated upon the addition of bicarbonate as the registered TON values for hydrogenation also increased from 13 373 to 102 593. Contrary to the case of potassium bicarbonate, NaHCO_3 does not impact catalysis favourably upon the loading increase. Sodium formate yields decrease and TON values calculated as the number of turnovers per that of catalyst molecules remain similar. These results might stem from the significantly higher solubility of potassium bicarbonate compared to NaHCO_3 that would result in a higher ionic strength of the aqueous phase throughout catalysis. Considering that identical catalyst loadings were used for all experiments depicted in Fig. 2, our data implies that the selection of the alkali cation is crucial for producing efficient catalytic systems.

Finally, we examined the impact of reaction conditions on the performance of the biphasic catalytic system. Varying the reaction temperature and pressure over a series of experiments (Fig. 3 and ESI†) we confirmed that biphasic hydrogenation exhibits behavior similar to that of single solvent systems. Namely, the increase of the reaction temperature from 65 to 120°C leads to a marked drop in formate yield, while the increase of H_2 pressure from 5 to 60 bar H_2 results in increased formate yield. This is consistent with the expected thermodynamic behavior of the system as well as recent reports detailing this reaction.⁴⁸

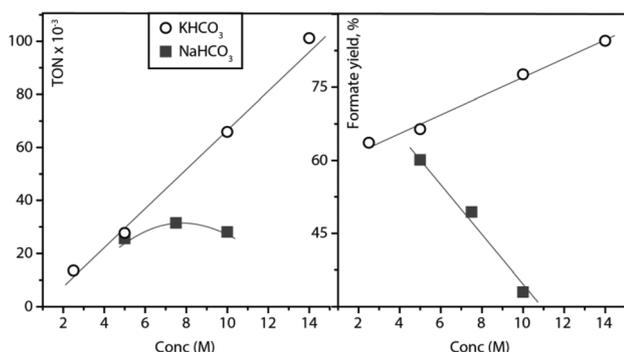


Fig. 2 Concentration effects of KHCO_3 and NaHCO_3 on the formate yield and TONs. Reaction conditions: 2 mL of solvent total ($\text{H}_2\text{O}/\text{toluene} = 1/1$), $0.107 \mu\text{mol}$ catalyst **1**, 0.055 mmol methyltrioctylammonium chloride, $T = 90^\circ\text{C}$, $p = 40 \text{ bar}$ ($p_{\text{H}_2} = 40 \text{ bar}$), $t = 4.5 \text{ h}$, concentrations are considered as $\text{M}/\text{H}_2\text{O}$.

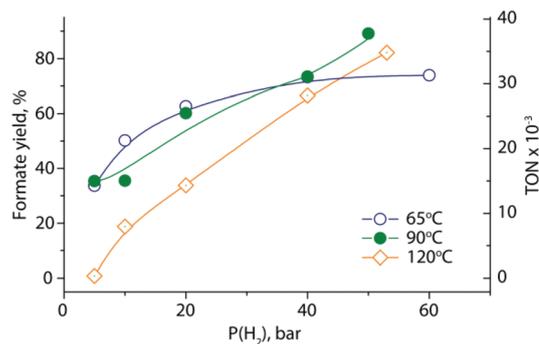


Fig. 3 Effect of temperature and pressure on the formate yield and TONs in the hydrogenation of KHCO_3 . Reaction conditions: 2 mL of solvent, $0.107 \mu\text{mol}$ catalyst **1**, 55 mM methyltrioctylammonium chloride, $t = 16 \text{ h}$, $\text{KHCO}_3 = 5 \text{ mmol}$, T and p are varied.

Examining the kinetics of bicarbonate hydrogenation we found that **1** is capable of developing high turnover frequencies (TOFs) with no apparent inhibition often observed in organic media.⁴⁹ Tracking hydrogen consumption in the course of hydrogenation we estimated the initial TOF to be in the extent of $73\,000 \text{ h}^{-1}$ (Fig. 4) with kinetic traces following a regular monoexponential trendline. These experiments could also confirm the ease of scaling this reaction that was performed at the 50 mmol scale as compared to a five-fold lower scale used in screening.

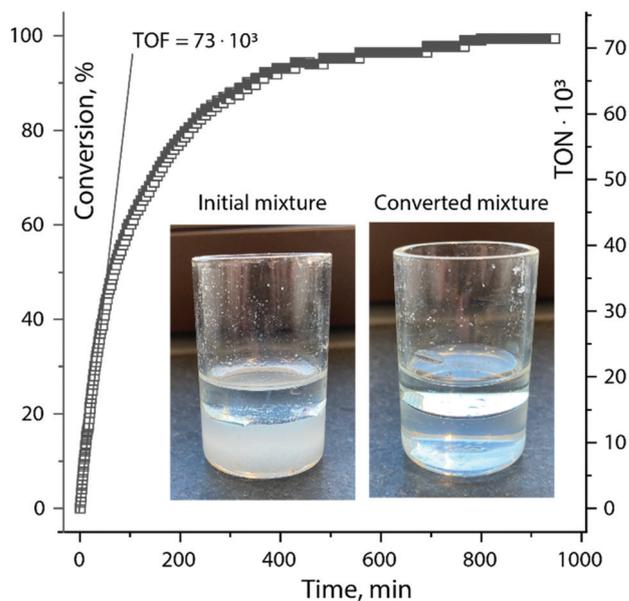


Fig. 4 Conversion versus time in the hydrogenation of KHCO_3 . Reaction conditions: 10 mL of solvent ($\text{H}_2\text{O}/\text{toluene} = 1/1$), $0.535 \mu\text{mol}$ catalyst **1**, methyltrioctylammonium chloride, $T = 90^\circ\text{C}$, $p = 50 \text{ bar}$ ($p_{\text{H}_2} = 50 \text{ bar}$), $\text{KHCO}_3 = 50 \text{ mmol}$ (10 M in H_2O). Inside the graph are the stirred reaction mixtures before (left) and after (right) reaction, showing the net conversion of the bicarbonate suspension into a clear solution at RT.



Table 4 Effect of the concentration of catalyst on the final yield and TON^a

Entry	Cat. (μmol)	TON	Yield (%)
1	0.006	474 026	55
2	0.012	296 756	70
3	0.029	109 224	64
4	0.059	56 996	67
5	0.12	27 728	67

^a Reaction conditions: 2 mL of solvent, 5 mmol KHCO_3 , $T = 90\text{ }^\circ\text{C}$, $p_{\text{H}_2} = 40\text{ bar}$, 0.055 mmol methyltrioctylammonium chloride, $t = 18\text{ h}$.

Finally, we probed the performance limits of the biphasic catalytic system based on **1**. In order to maximize TON per batch we varied the catalyst concentration and found no significant productivity drop with the catalyst concentration as low as 2 ppm with respect to the bicarbonate substrate (Table 4). Under these conditions, TON values up to 300 000 can be achieved with similar formate yields in the extent of 70%, producing clear formate solutions at the end of the catalytic reaction.

Conclusions

To conclude, in this work we developed a potent catalytic system based on ruthenium complex **1**. Making use of its biphasic composition, our system is capable of converting supersaturated bicarbonate slurries to formate solutions close to their saturation point. We demonstrate the generation of *ca.* 50%_w aqueous formate solutions from commercial potassium bicarbonate with no substrate purification required prior to catalysis. With a maximum TON of 474×10^3 catalyst **1** appears very promising for developing intense hydrogenation processes in aqueous medium free of the limitations associated with conventional organic solvents.

Author contributions

CR performed investigation and data analysis and developed the methodology; GA and EAP contributed to project management, supervision and data analysis; EAP provided resources; all authors wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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