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An all-aqueous and phosphine-free integrated amine-assisted CO_2 capture and catalytic conversion to formic acid†

Ritu Bhardwaj, Abhishek Kumar and Joyanta Choudhury 🆔 *

A phosphine-free Ir(III)-NHC-based efficient catalytic system is developed for integrated CO_2 capture with tetramethylguanidine as a capturing agent and conversion to formate with H_2 gas, conducting both the steps in water, affording product yield up to 85% and TON up to 19 171 in just 12 h. In the segment of "integrated CO_2-capture and conversion to formate", this system represents not only the first phosphine-free module, but also one of the few best known homogeneous catalysts.

CCS (Carbon Capture and Sequestration) and CCU (Carbon Capture and Utilization) are two processes holding immense importance in the critical need for the removal of CO_2 from industrial sources and air.[1–3] The advantageous CCU process can be deployed to convert CO_2 (captured from air) into important value-added chemicals including fuels, materials, and polymers (Fig. 1).[4–6] The conversion of CO_2 to fuels such as formic acid or methanol is particularly attractive because it can cater to the growing demand for energy.[7] Formic acid is a simple organic acid with numerous applications. To name a few, it is used in textile processing, industrial cleaning, acidification of food and water serving animal nutrition, and de-icing. Furthermore, formic acid is a promising hydrogen energy carrier owing to its liquid nature and high volumetric capacity (53 g H_2 L^{-1}).[8] Also, its application in generating electricity through direct formic acid or formate fuel cells has been demonstrated.[9,10] Thus, the need to develop efficient CO_2-hydrogenation catalysts that function well with CO_2 capture systems to give formic acid/formate is highly justified. Amines have been extensively employed to chemically absorb CO_2 in the industrial setup for many decades.[11] The first report of integrated CO_2 capture and conversion to formate utilizing amines was detailed by the He group in 2013 wherein they demonstrated polyamine and amidine-based CO_2 capture

in an alcoholic solvent and conversion to formate using an Rh-phosphine catalyst.[12] In this pioneering work, they were able to obtain the turnover number (TON) of 726 (in 16 h), using 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in glycol as the capturing agent. Later, they improved their results by utilizing ethoxy-functionalized amidine and potassium phthalimide-based capture systems.[13] Following these developments, Heldebrant and co-workers reported CO_2 capture by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in methanol and subsequent conversion to formate using a $RuCl_2(PPh_3)_3$ catalyst giving a TON of 5100 (in 40 h).[14] In 2014, McNamara and Hicks reported a multifunctional polyethyleneimine (PEI)-tethered catalyst for CO_2 capture and conversion to formate.[15] In 2016, the Prakash group, for the first time, detailed CO_2 capture in an aqueous amine solution (amine = tetramethylguanidine, TMG) and subsequent hydrogenation to formate utilizing Ru-PNP pincer catalysts to obtain a TON > 7000 (in 20 h) for formate from captured CO_2-TMG adduct.[16] In 2017, Francio, Leitner and co-workers reported an integrated process for the synthesis of formate amine adduct using methanolamine and $[RuCl_2(dppm)_2]$ (dppm: 1,1-bis(diphenylphosphino)-methane) as the catalyst.[17] In 2018, Huang and co-workers showed that with pentamethyldiethylenetriamine (PMDTA), CO_2 from the air can be captured and converted efficiently to ammonium formate salts over multiple cycles using a Ru-PN³P pincer catalyst.[18] In 2021, the Beller group demonstrated a CO_2 capture and utilization strategy based on amino acid, L-lysine, and water reporting TON > 50 000 (in 12 h) for the formate product with the help of a Ru-MACHO-BH catalyst.[19] Recently, the L-lysine-based method was further
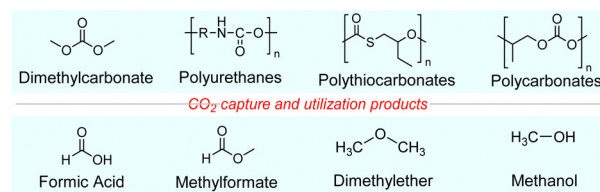
Organometallics & Smart Materials Laboratory, Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal 462066, India. E-mail: joyanta@iiserb.ac.in

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Fig. 1 Various value-added products of CO_2 capture and utilization (CCU) processes.

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improved by the Beller group using an Mn-PNP-pincer catalyst, to afford the maximum TON value of 230 000, conducting the reaction in THF/water.[20] A closer look at the reported systems disclosed some key observations regarding these CCU processes. All the reported systems utilize phosphine-based ligands. Although phosphine-based metal complexes have achieved great success in hydrogenation reactions, some impediment is always associated with their handling and use.[21] Generally, handling of such catalysts under inert gas and in degassed solvents is essential while performing catalytic reactions, to avoid the commonly encountered unwanted oxidation of the phosphine ligands. Secondly, in all of the developed systems, while both organic solvent and H_2O were used for the CO_2-capture step, the CO_2-conversion step invariably needed to be operated in mixed organic-aqueous solvents. It has been previously reported that the good solubility of the in situ-formed carbamate and/or bicarbonate/carbonate species in the aqueous phase enhances the reaction rate in homogeneous catalytic systems.[22] Based on these analyses, it is clear that developing air-stable, easily-handleable, non-phosphine ligand-based metal catalysts applicable for integrated CO_2 capture and conversion processes is a desirable goal from a practical operational point of view. In addition, the CCU process using H_2O as the 'green' solvent for both CO_2 capture and CO_2 conversion steps still remains a future goal. With this background, we sought to develop an efficient CCU strategy employing a non-phosphine ligated transition metal catalyst system, for conversion of CO_2 to formate in aqueous media, facilitated with an amine-assisted CO_2 capture step in water as well (Fig. 2). The catalyst design principle for this purpose involved the implication of chelating an N-heterocyclic carbene (NHC) ligand as the substitute for the phosphine-based one. NHCs serve as a versatile class of strong σ-donor ligands in transition metal-based several hydride-transfer catalyses. Our group previously utilized NHC-based Ir/Ru catalysts for the reduction of various organic compounds such as imines, aldehydes, ketones, and N-heteroarenes.[23–25] Importantly, hydride-transfer protocols in CO_2 hydrogenation and transfer hydrogenation were also developed utilizing a 'benzimidazolato-abnormal NHC'-based Ir complex ([Ir]^{imd}, Fig. 2B).[26–28] In the current context, notably, the complex [Ir]^{imd} was found to be air-stable, and could be handled without the strict maintenance of an inert atmosphere even in the solution state, thus opening an opportunity to apply it in the proposed all-aqueous integrated CCU process (Fig. 2B).

The CO_2 capture capacity of various aqueous amine solutions has previously been detailed by a few groups.[29] In our investigation, we utilized a simple technique of sequestering CO_2 into the aqueous amine solution in a closed vessel under ambient conditions (see ESI† for details). The identification of the nature of the captured product was performed via ^{13}C NMR spectroscopy. The captured products have been characterized as a mixture of carbamate/bicarbonate/carbonate depending on the degree of the amine group; primary amine groups form both carbamate and bicarbonate/carbonate products while tertiary and secondary amine groups generate only bicarbonate/carbonate products. The estimation of the amount of CO_2 captured in the solution was done using the standard gravimetric technique in line with previous reports. We found that pentaethylenehexamine (PEHA) proved to be an efficient polyamine for CO_2 capture displaying a CO_2 capture capacity of 2.50 mmol CO_2 per mmol amine (Table 1, entry 1). Other amines such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), tetramethylguanidine (TMG), 1,4-diazabicyclo[2.2.2]octane (DABCO), methanolamine (MEA), pentamethyldiethylenetriamine (PMDTA), and amino acid ʟ-lysine displayed good to excellent capture efficiency as well (Table 1, entries 2–7). A representative ^{13}C NMR spectral profile of the aqueous solution containing CO_2-captured TMG suggested the existence of bicarbonate/carbonate salts of the amine (Fig. 3).

Next, we investigated the [Ir]^{imd}-catalyzed aqueous-phase hydrogenation of the captured-CO_2 as obtained in the aqueous amine solutions described above in Table 1. The respective aqueous solutions containing the CO_2-captured product were subjected to hydrogenation under 50 bar H_2 pressure at 120 °C for 8 h in the presence of a catalytic amount of [Ir]^{imd} in water
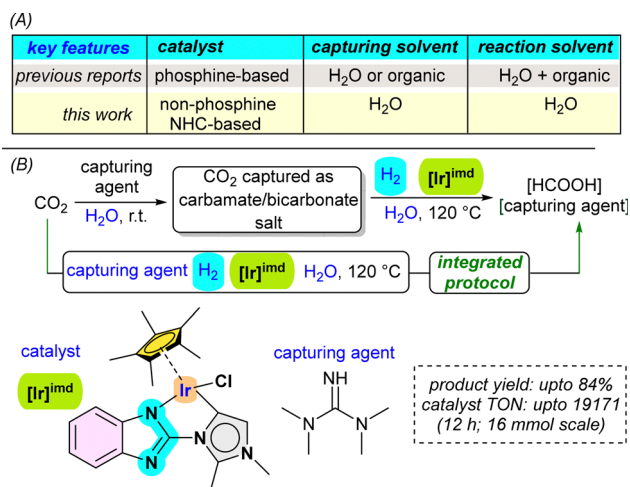
Fig. 2 (A) Key features of the reported systems for integrated CO_2 capture and conversion to formate utilizing amines as capturing agents, and the system developed in this work. (B) The present work showing the capturing agent and the catalyst.

Table 1 CO_2 capture by aqueous amine solutions[a]

#	Amine	mmol CO_2 captured	mmol CO_2/g amine	mmol CO_2/mmol amine
1	PEHA	11.0	11.47	2.50
2	DBU	6.2	6.3	0.96
3	TMG	7.6	8.3	0.97
4	DABCO	8.0	7.9	0.88
5	MEA	11.0	11.1	0.68
6	PMDTA	8.0	7.27	1.26
7	ʟ-lysine	7.5	5.07	0.75

[a] The following amounts of amines were dissolved in 3 mL of water: PEHA = 1.04 g (4.4 mmol), DBU = 0.98 g (6.4 mmol), TMG = 0.91 g (7.9 mmol), DABCO = 1.00 g (8.9 mmol), MEA = 0.98 g (16.2 mmol), PMDTA = 1.10 g (6.3 mmol), ʟ-lysine = 1.48 g (10.0 mmol). The amount of CO_2 captured was given for the duration of 1 h at room temperature. Experiments were performed at least thrice; average values are used and are within <5% error.
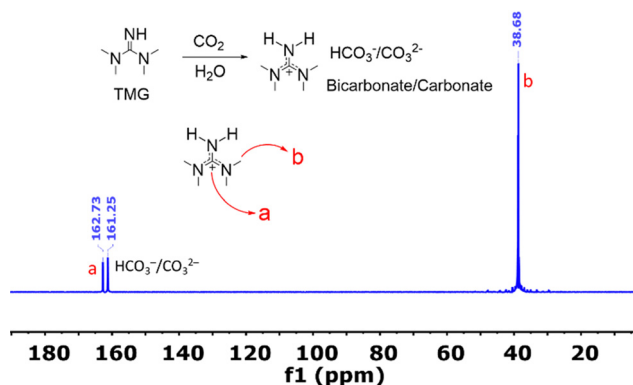
Fig. 3 $^{13}C\{^1H\}$ NMR spectrum of the CO_2-captured TMG species in an aqueous solution.

Fig. 4 $^{13}C\{^1H\}$ NMR spectrum of the product mixture for the conversion of the CO_2-captured TMG species in aqueous solution.

(Table 2, entries 1–8). In all cases, the formic acid adduct of the respective amine (or the corresponding ammonium formate) was obtained as the product, analysed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in D_2O. Thus, 44% product yield with a TON value of 1132 was obtained when 11 mmol of CO_2 captured by PEHA was charged with 4.3 μmol of catalyst loading (Table 2, entry 1). In the case of the superbases (DBU, TMG, and DABCO) as the capturing agents, conversion of the TMG-captured CO_2 under identical catalytic conditions was the highest, providing 85% product yield with a catalytic TON value of 1483 in 8 h, as compared to %yield and TON of 76% and 1100 for DBU and

65% and 1216 for DABCO, respectively (entry 3 *vs.* entries 2 and 4). For MEA- and PMDTA-captured CO_2, higher TON values were obtained than for TMG-captured CO_2, but the yields of the corresponding products were lower (entries 5 and 6). On the other hand, for L-lysine-captured CO_2, both the product yield (71%) and catalyst's TON value (1249) were relatively lower (entry 7). Thus, from the above screening analysis, TMG was considered to be the optimum amine for the current CCU protocol, for further investigation. A typical ^{13}C NMR spectrum of the aqueous solution containing the product mixture for the conversion of the CO_2-captured TMG indicated the presence of the formic acid adduct of TMG (or formate salt of TMG) (Fig. 4). Next, the effect of reaction time was scrutinized for TMG (entries 8–10, Table 2 and Fig. 5). When the hydrogenation reaction was conducted for 1 h, 3 h, and 4 h duration (instead of 8 h) under otherwise identical reaction conditions, it was observed that the product yield reached the value 83% in just 4 h (entry 10). The time-dependent ^1H NMR spectroscopic monitoring profile confirmed the gradual increase of the formate peak with time (Fig. 5A), along with the increase of the TON value in a linear manner up to 3 h where the product yield

Table 2 Homogeneous hydrogenation of amine-captured CO_2[a]

#	Amine	Captured CO_2 (mmol)	Catalyst (μmol)	Time (h)	Yield (%)	TON
1	PEHA	11	4.3	8	44	1132
2	DBU	6.2	4.3	8	76	1100
3	**TMG**	**7.6**	**4.3**	**8**	**84**	**1483**
4	DABCO	8.0	4.3	8	65	1216
5	MEA	11.0	4.3	8	60	1542
6	PMDTA	8.0	4.3	8	80	1494
7	L-Lysine	7.5	4.3	8	71	1249
8	TMG	7.6	4.3	1	62	1100
9	TMG	7.6	4.3	3	82	1456
10	**TMG**	**7.6**	**4.3**	**4**	**83**	**1464**
11[b]	TMG	7.6	4.3	3	6	114
12[c]	TMG	16.0	8.8	4	80	1463
13[c]	TMG	16.0	8.8	8	83	1520
14[c]	TMG	16.0	2.0	20	70	5600
15[c]	**TMG**	**16.0**	**2.0**	**30**	**76**	**6142**
16[d]	**TMG**	**4.4**	**4.3**	**4**	**82**	**837**

[a] Reaction conditions: CO_2 captured product as substrate (following the procedure from Table 1), 7 mL additional water, H_2 (50 bar), catalyst [**Ir**]^{imd} = as mentioned, temp. = 120 °C, time = as mentioned. The amount of formate was determined by ^1H NMR spectroscopy using imidazole as the internal standard. [b] Reaction done at 70°. [c] 17 mmol of TMG was used in the capture step. [d] 7.9 mmol TMG was used to capture CO_2 from air over a period of 72 h. Each experiment was performed at least three times; average values of %yield and TON are used and are within <5% error.
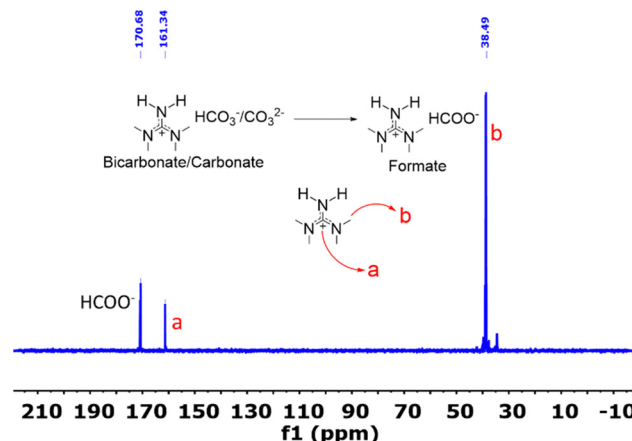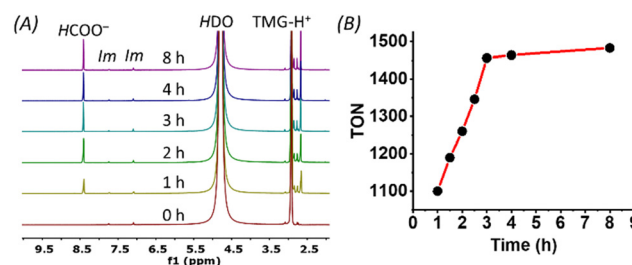

Fig. 5 (A) Time dependent ^1H NMR spectra of the standard hydrogenation reaction of the CO_2 captured product from TMG in D_2O. Reaction conditions: 7.6 mmol CO_2 captured product, H_2 (50 bar), 4.3 μmol [**Ir**]^{imd} catalyst, temp. = 120 °C. Im denotes the peaks due to the aromatic H's of the internal standard imidazole. TMG-H$^+$ denotes the peak due to the N–CH_3 protons of the protonated TMG. (B) Corresponding time-dependent reaction profile (TON *vs.* time) of the same reaction.
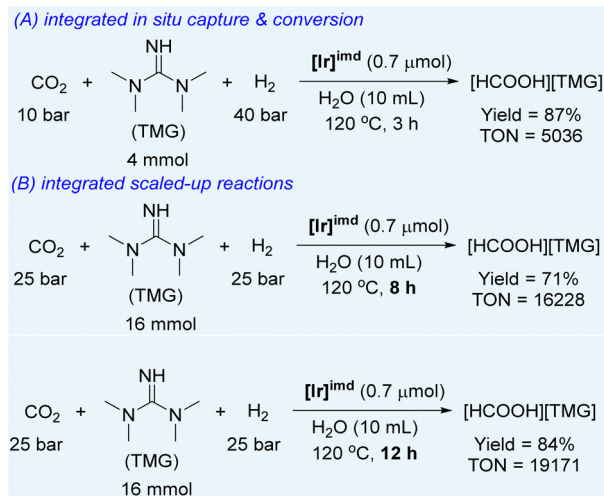
Fig. 6 Integrated one-step *in situ* CO_2 capture and hydrogenation protocol in water using TMG as the capturing agent and [**Ir**]^{imd} as the catalyst.

nearly stabilized (entry 9, Table 2, and Fig. 5B). Lowering the reaction temperature decreased the performance (entry 11).

Next, with TMG as the CO_2-capturing amine, a scaled-up reaction was conducted by charging 16 mmol of TMG-captured CO_2 and 8.8 µmol of [**Ir**]^{imd} for 4 h under identical conditions. Delightedly, both the product yield (80%) and catalyst TON value (1463) were found to be maintained (entry 12) as in the half-scale reaction (entry 10). Extending the reaction to 8 h improved the yield and TON a bit (entry 13). Significantly, under these scaled-up reaction conditions (16 mmol substrate), lowering of the catalyst loading to just 2.0 µmol still produced a high yield (70–76%) of product, furnishing TON values of 5600 and 6142 in 20 h and 30 h, respectively (entries 14 and 15, Table 2). These results suggested that [**Ir**]^{imd} is an efficient catalyst for the hydrogenation of TMG-captured CO_2 to formic acid under aqueous conditions for obtaining both high product yield and high TON value. Finally, CO_2 from atmospheric air was captured by an aqueous TMG solution and the captured-CO_2 was hydrogenated to formate efficiently (yield 82%) (entry 16, Table 2).

After successful stepwise CO_2-capture with TMG as the optimum amine and CO_2-conversion with [**Ir**]^{imd} as the hydrogenation catalyst, executing both the steps in water, we tested the feasibility of an integrated one-step *in situ* capture and conversion protocol. As depicted in Fig. 6, a mixture of 10 bar of CO_2 gas, 4 mmol of TMG and 40 bar of H_2 gas in H_2O was charged with 0.7 µmol loading of [**Ir**]^{imd} catalyst, and the consecutive capture and conversion reaction was conducted at 120 °C for just 3 h. Interestingly, 87% yield of formic acid product with the catalytic TON of 5036 was achieved, signifying an efficient integrated protocol (Fig. 6A). This integrated protocol was tested further for its efficacy with scaled-up setup. For 16 mmol (1.84 g) of TMG and 25 bar of CO_2, under 25 bar H_2 pressure at 120 °C, the catalyst with 0.7 µmol loading performed efficiently and furnished 71–84% of the product within 8–12 h, reaching the TON value of 19 171 in 12 h (Fig. 6B).

In conclusion, we have demonstrated an efficient integrated CO_2 capture and conversion system in a completely aqueous solution using a tailored Ir-NHC-based catalyst, for the production of formic acid. Superbase TMG was found to be the most efficient for the process providing an excellent yield of $\sim$85% and TON value reaching 19 171. Thus, in the segment of "integrated CO_2-capture and conversion to formate", the system developed herein, represents not only the first phosphine-free module but also one of the few best homogeneous catalysts reported in the literature.[19,20]

Conflicts of interest

There are no conflicts to declare.

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