Integrated carbon capture and utilization to methanol with epoxide-functionalized polyamines under homogeneous catalytic conditions

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A B S T R A C T

Herein, a novel amine based integrated process is presented for CO_2 capture and utilization (CCU) to synthesize methanol. Reaction of pentaethylenehexamine (PEHA) with selected epoxides led to a library of functionalized polyamines. In aqueous medium, the modified amines were efficient in capturing CO_2 under ambient conditions. Subsequently, the CO_2 loaded solutions were directly subjected to catalytic hydrogenation to CH_3OH in presence of molecular H_2 and Ru-PNP based molecular catalysts. While the epoxide-modified amines exhibited CO_2 capture efficiencies comparable to those of unmodified PEHA, they displayed a notable enhancement in the hydrogenation step resulting in higher methanol yields of up to 93%. Furthermore, the integrated process was demonstrated in a water and 2-methyl-THF based biphasic solvent system. We believe that the improved amine-based system for CO_2 capture and hydrogenation to methanol is key in advancing low temperature and renewable methanol synthesis processes.

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1. Introduction

With the objectives of achieving carbon neutrality and a circular economy, recent years have witnessed the emergence of CO_2 capture and recycling or utilization models (CCR or CCU), wherein CO_2 released from various anthropogenic sources is captured and directed downstream as a C-1 building block for the production of a multitude of value-added chemicals and materials [1–3]. Distinct from the more conventional carbon capture and storage (CCS) technologies, CCU processes can collectively address the issues and challenges relevant to increasing CO_2 emissions as well as offer renewable carbon sources for fuels and feedstocks with low-carbon footprints [4–6].

Among the various chemicals accessible from CO_2, methanol (CH_3OH) is one of the most attractive products [7]. It is the simplest alcohol, a convenient one-carbon liquid at room temperature that is easy to store, transport and dispense. It is a prominent building block to synthesize various commodity chemicals and materials such as acetic acid, formaldehyde, methyl–*tert*–butyl ether (MTBE), various polymers and pharmaceuticals. Industrially, methanol can also be catalytically converted to a variety of hydrocarbons and olefins such as ethylene, propylene, gasoline etc.

via the methanol-to-olefin (MTO) and methanol-to-gasoline (MTG) processes [8]. Methanol from CO_2 is an excellent green substitute as a direct drop-in fuel (M100) and as an additive to gasoline (M15, M85). In essence, most of the hydrocarbon-based chemicals and fuels presently obtained in an unsustainable manner can be derived from methanol. The "methanol economy" when coupled with renewable methanol synthesis through CO_2 recycling, has the power to pave the way for a sustainable and fossil-independent future [9].

Methanol is already produced at a scale of over 100 million MT per year to supply the vast and rapidly growing global market [5]. At present, methanol is majorly derived from fossil fuel resources (natural gas and coal) via an industrial catalytic process through syngas which is mainly comprised of CO and H_2. However, novel routes to access methanol from renewable carbon sources including biomass, biogas and carbon dioxide are desired. Particularly, methanol can be synthesized from CO_2 in the presence of high pressures of H_2 and copper based heterogeneous catalysts at high temperatures of 250 to 300 °C, although with a relatively low conversion of about 30% per cycle due to intrinsic thermodynamic limitations of the reaction [10,11]. Over the past decade, there has been growing interest in the search for alternate low temperature CO_2 to methanol processes, with notable advances in hydrogenation systems enabled by highly efficient and selective molecular catalysts [12–14]. Operating under mild homogeneous conditions, the catalysis has been shown to proceed in the presence of alcohol

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or amine additives, as well as in some cases under additive free conditions [15–19].

Significant advances have been achieved in the field of amine-assisted routes for CO_2 to methanol (Scheme 1) initiated by seminal studies including those by the groups of Milstein, Sanford, Ding and Olah/Prakash [20–30]. Operating under basic conditions, the catalytic hydrogenation proceeds through key intermediates with the corresponding amine: ammonium carbamates/bicarbonates, ammonium formates and formamides (Scheme 1B). In parallel, amine-based adsorbents/absorbents are also being widely deployed for state-of-the-art CO_2 capture technologies, hence making such systems potentially useful in developing CCU processes [31–34]. In this direction, our group as well as others have demonstrated initial examples of an *integrated capture and conversion* strategy [25,35–43]. The advantage of a one-pot integrated CCU process is that it essentially eliminates the desorption and compression steps. These two steps are otherwise necessary to strip off the absorbed CO_2 and store it under pressure for further use in conventional non-integrated processes. Hence, the proposed process not only combines two processes, but is also step-economical.
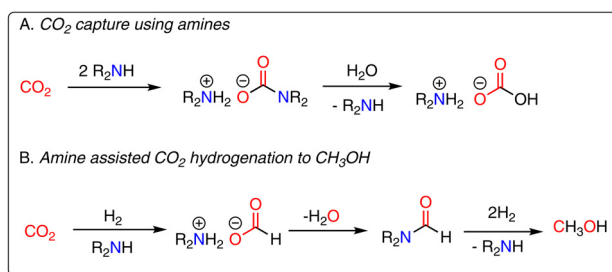
Scheme 1. Amine based CO_2 capture and hydrogenation.

There are limited examples of amine assisted CO_2 capture and hydrogenation to methanol to date. While these systems have contributed to the fundamental understanding of the catalytic pathways, the amines used in such studies have relatively low boiling points and significantly high vapor pressures [40]. Hence, they often suffer from volatility issues as well as degradation over several cycles under the reaction conditions [44]. As part of our enduring research to develop stable, efficient and cost-effective amine based systems, we report herein, a focused array of easy-to-prepare epoxide-functionalized polyamines and demonstrate their utility in an integrated CO_2 capture and hydrogenation system to synthesize CH_3OH. The catalysis is enabled by highly efficient and commercially available ruthenium based PNP pincer catalysts under relatively mild conditions of 140–145 °C.

2. Results and discussion

Amine based CO_2 scrubbing technologies are well established and commonly practiced on a large scale to strip CO_2 from effluent gas streams in industrial processes [45]. In a typical "capture" reaction of CO_2 with amines, primary and secondary amine functionalities can form the corresponding ammonium carbamate ion pairs with CO_2 with a maximum amine efficiency (moles of CO_2 absorbed per mole of amine moiety) of 50% (Scheme 1A). Introducing water either as a solvent or humidity in the gas stream can enhance the CO_2 capture efficiency through the formation of the corresponding ammonium bicarbonate with a 1:1 stoichiometric ratio between amine and CO_2. In contrast to primary and secondary amines, tertiary amino groups lacking -NH proton only react with CO_2 in the presence of water. The use of amines with high boiling points, low volatility and rich in amine content is highly desired. In this regard, branched and linear polyethylen-

imines (B/L-PEI) have been the focus of numerous CO_2 capture studies [46–48]. While such polyamines are commercially available in bulk, their complex mode of production leads to significantly high prices and hence, restricting the scale-up of PEI based technologies [49]. Additionally, in our previous study, we found that PEIs were inefficient for methanol synthesis in an integrated CCU system [41]. As an alternative, shorter polyamine chains such as pentaethylenehexamine (PEHA) or tetraethylenepentamine (TEPA) that are produced at much lower bulk price have been shown to be efficient in both CO_2 capture as well as CO_2 hydrogenation processes [25,50–51]. However, even these high boiling amines pose major challenges in terms of volatility, atmospheric contamination as well as degradation under thermal and oxidative conditions [52–53]. Recently, Goeppert, Prakash et al. developed solid supported adsorbents using PEHA while effectively addressing these drawbacks [54]. In that study, amines were treated with epoxides such as propylene oxide (PO) and butylene oxide (BO) increasing their molecular weight and sharply decreasing their vapor pressure. The epoxide-functionalized amines demonstrated high capture efficiencies and regenerability. Most importantly, relative to their unmodified equivalents these materials displayed remarkable stability even under harsh operating conditions with negligible loss of capture efficiencies over multiple adsorption-desorption cycles. However, application of epoxide-modified polyamines in liquid phase for CO_2 capture as well as for CO_2 hydrogenation has yet to be explored.

In the present study, we selected PEHA as a model polyamine with high content of primary and secondary amino groups. The modification of PEHA with various epoxides was carried out by a simple and scalable process at room temperature in aqueous phase [55]. Water is the ideal reaction solvent, being environmentally benign and economic. The selected epoxides are liquids at room temperature and can be handled conveniently. In general, ring opening reaction of the oxirane with amine leads to formation of the corresponding β-amino-alcohol species. Hence, the modification of PEHA with an epoxide essentially converts a fraction of the amino groups to the corresponding amino-alcohols (Scheme 2). For a molar ratio of 1:1 for PEHA and epoxide, a statistical distribution of products is obtained with a major probability of reaction products with 1:1 PEHA/epoxide (a mixture of regio-isomers), although minor fractions with multiple epoxide functionalization may also be present [54]. Further, the content of secondary and tertiary amino groups in PEHA is increased as a result of functionalization.

For CO_2 capture, a polar protic solvent with high solubility for the amines as well as the capture products is desired. Hence, water was selected as the capture solvent in the present study, also owing to its key role in enhancing the CO_2 capture efficiency for amines, as stated *vide supra*. When an aqueous solution of PEHA-1PO (reaction product of PEHA with one equivalent propylene oxide) was subjected to CO_2 at ambient temperature and atmospheric pressure, 3.3 mmol of CO_2 was captured per mol of PEHA-1PO with a high amine efficiency of 0.55 CO_2/N (Table 1, entry 2). ^{13}C NMR of the CO_2 loaded amine solution showed the presence

Table 1

CO_2 capture by aqueous solutions of epoxide-functionalized PEHA.[a]

Entry	Amine	CO_2 captured (mmol)[b]	CO_2/N[c]
1	PEHA	3.5	0.58
2	PEHA-1PO	3.3	0.55
3	PEHA-2PO	3.1	0.52
4	PEHA-1TFPO	3.0	0.50
5	PEHA-1BO	3.0	0.50
6	PEHA-1CPO	2.2	0.37

[a]Capture conditions: PEHA or PEHA-epoxide (1.0 mmol), water (5 mL), stirring (800 rpm.), rt, $t = 1$ h. [b]Captured CO_2 amounts determined gravimetrically. [c]moles of CO_2 captured per mole of nitrogen. Calculation error ±5%.
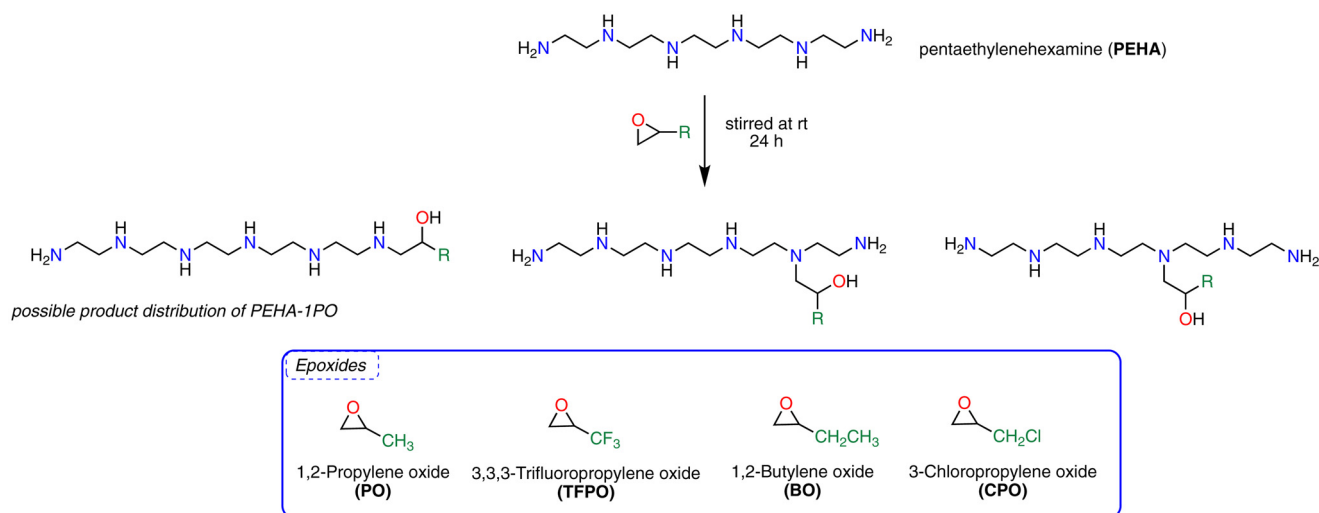
Scheme 2. Functionalization of PEHA with various epoxides.

of carbamate and bicarbonate ion pairs supporting our observations from previous studies with aqueous amines [41]. The activity of PEHA-1PO was comparable to that of unmodified PEHA in water (CO_2/N = 0.58, entry 1). With PEHA-2PO, the capture efficiencies decreased slightly to 3.1 mmol of CO_2 (CO_2/N = 0.52, entry 3), which can be accounted for by the increased bulkiness of the polyamine as well as higher content of tertiary amino groups, which have kinetically lower efficiencies for CO_2 capture. Apart from PO, the effect of other epoxides was explored for PEHA functionalization. PEHA-1BO (BO = 1,2 butylene oxide) and PEHA-1TFPO (TFPO = 3,3,3-trifuoropropylene oxide) both exhibited CO_2 capture efficiencies of 0.50 CO_2/N, possibly due to minor stereoelectronic and steric effects of the substituents (entries 4–5). However, in case of PEHA-1CPO (CPO = 3-chloropropyleneoxide or epichlorohydrin), a drastic decrease in the CO_2 capture activity was observed (CO_2/N = 0.37, entry 6).

To integrate CO_2 capture and its subsequent conversion, the CO_2 loaded amine solutions were directly subjected to hydrogenation in the presence of a Ru based molecular catalyst and H_2 gas. An efficient protocol for reduction of CO_2 capture species with amines to methanol was developed by our group previously [25,41]. It is important to note here that while water is an ideal solvent for the CO_2 capture step, the Ru-complexes used in the catalysis step have minimal solubility in water. Hence, a compatible co-solvent was introduced to form a homogeneous reaction system. The molecular catalysts selected in the present study have been extensively employed for reduction of carbonyl compounds and more recently, for CO_2 to CH_3OH catalytic systems [13,56–60].

Using THF as the co-solvent and Ru-Macho-BH (C-1) as the catalyst, the aqueous solution of CO_2 loaded PEHA (3.6 mmol CO_2) was subjected to hydrogenation at 140 °C under 70 bar of H_2 (Table 2, entry 1). After 20 h, 1.1 mmol CH_3OH was obtained corresponding to 31% yield with respect to the captured CO_2. When CO_2 captured in aqueous PEHA-1PO solution was subjected to a similar reaction condition, the methanol yield increased significantly to 47% (entry 2). Increasing the volume of THF had no distinct effect on the methanol production (entry 3). With ethylene glycol as a co-solvent, methanol yield decreased to 28% (entry 4). After the reaction completion, the catalyst was found to be only partly soluble in the highly polar water-ethylene glycol solvent system. When the co-solvent was switched to triglyme, a high boiling and green ethereal solvent, methanol yield improved markedly to 59% in 20 h (entry 5). Similar to C-1, Ru-Macho (C-2) was comparably active for hydrogenation with a 56% yield for CH_3OH (entry 6). However, a

negligible CH_3OH yield of 9% was obtained with C-3 as the catalyst (entry 7). The observed trend in the catalytic activities is in strong correlation with our recent insights into the mechanism of amine assisted CO_2-to-CH_3OH in which the P-substituent in the PNP ligand of the catalyst was found to influence the CH_3OH yield significantly [27]. Finally, with a slight manipulation of the reaction parameters to 145 °C and 80 bar of H_2, the methanol yield could be enhanced to 72% in 20 h and further to a high yield of 91% within 48 h (entries 8–9). Apart from CH_3OH, formate ($HCOO^-$) and trace formamide (N–CHO) intermediates were also accumulated during the hydrogenation reactions.

Under these optimized conditions for hydrogenation of CO_2 to CH_3OH with PEHA-1PO, other CO_2 loaded polyamines were also subjected to the catalytic reduction. With PEHA-2PO, the hydrogenation efficiency dropped to a certain extent with a CH_3OH yield of 77% (entry 10). A similar effect was observed in the case of PEHA-1BO affording a CH_3OH yield of 83% (entry 11). However, a prominent decrease in CH_3OH production was observed in the hydrogenation of CO_2 captured with PEHA-1CPO and a moderate yield of 41% was achieved for CH_3OH (entry 12). Interestingly, the catalytic hydrogenation of captured CO_2 was quite efficient in presence of PEHA-1TFPO leading to a high CH_3OH yield of 93% (entry 13).

In-depth understanding of the overall reaction pathways in the catalytic hydrogenation of CO_2 to methanol is key for the further advancement of this process. Specifically, the role of the amine in the hydrogenation sequence has been studied previously by us as well as others (Fig. 1F) [27,29,61]. In an integrated CO_2-to-methanol process, amine plays dual roles in the CO_2 capture step as well as in the hydrogenation step. The modes of amine reactivity with CO_2 in the capture step has been discussed *vide supra*. In the hydrogenation step, amines mediate multiple key transformations during the catalytic cycle. First, amines promote dissolution of CO_2 gas, thus enhancing its abundance in the solution phase where the catalyst operates. Next, after the first reductive step of CO_2 to formate species, amine assists in detaching the formate anion (as ammonium formate) attached to the Ru-center as a ligand. This hypothesis is supported by our observation in a previous related study [27], in which CO_2 hydrogenation even to formate, was completely absent without an amine. Finally, amines with -NH protons undergo condensation with the ammonium formate to give a formamide intermediate and producing an equivalent of H_2O. This step is crucial in further reduction of the formate salt to CH_3OH.

Table 2

Catalytic hydrogenation of CO_2 captured by aqueous amine solutions.[a]
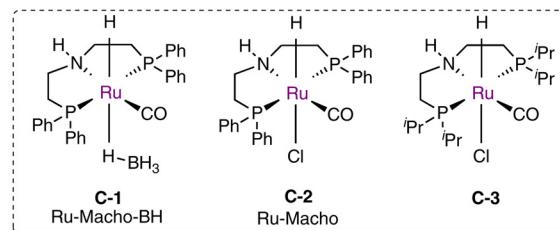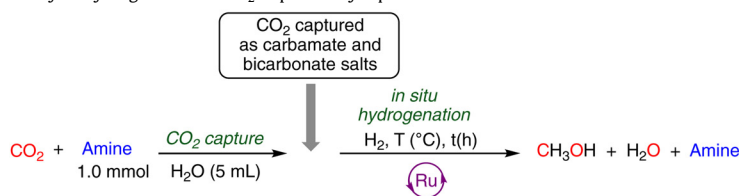
Entry	Amine	CO_2 captured (mmol)	catalyst (mol%)	co-solvent (mL)	T (°C)	H_2 (bar)	t (h)	formate (mmol)	CH_3OH (mmol)	CH_3OH (%)
1	PEHA	3.5	**C-1**(0.5)	THF(5)	140	70	20	0.8	1.1	31
2	PEHA-1PO	3.3	**C-1**(0.5)	THF (5)	140	70	20	0.6	1.4	42
3	PEHA-1PO	3.3	**C-1**(0.5)	THF (10)	140	70	20	0.6	1.4	42
4	PEHA-1PO	3.3	**C-1**(0.5)	ethylene glycol (5)	140	70	20	0.3	0.7	21
5	PEHA-1PO	3.3	**C-1**(0.5)	triglyme (5)	140	70	20	0.4	1.9	58
6	PEHA-1PO	3.3	**C-2**(0.5)	triglyme (5)	140	70	20	0.9	1.7	52
7	PEHA-1PO	3.3	**C-3**(0.5)	triglyme (5)	140	70	20	0.9	0.4	12
8	PEHA-1PO	3.3	**C-1**(0.5)	triglyme (5)	145	80	20	0.4	2.2	67
9	PEHA-1PO	3.3	**C-1**(0.5)	triglyme (5)	145	80	48	0.1	3.0	91
10	PEHA-2PO	3.1	**C-1**(0.5)	triglyme (5)	145	80	48	0.3	2.4	77
11	PEHA-1BO	3.0	**C-1**(0.5)	triglyme (5)	145	80	48	0.2	2.5	83
12	PEHA-1CPO	2.2	**C-1**(0.5)	triglyme (5)	145	80	48	0.2	0.9	41
13	PEHA-1TFPO	3.0	**C-1**(0.5)	triglyme (5)	145	80	48	0.2	2.8	93

[a]Reaction conditions: solutions from Table 1 (as specified) were directly hydrogenated, stirring at 800 rpm, pressures at rt. Yields calculated relative to CO_2 captured as determined by ^{1}H NMR. Calculation error ±5%.

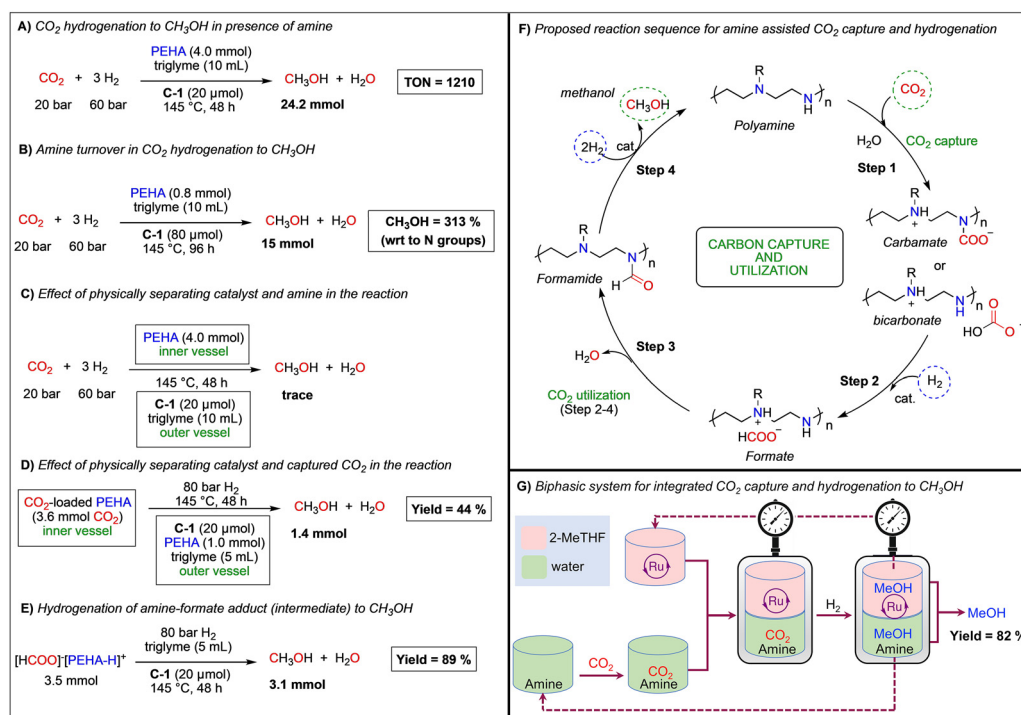**Fig. 1.** A-F) Investigations to probe the proposed mechanism of CO_2 hydrogenation and the role of amine, G) Demonstration of biphasic system for CO_2 capture and conversion, Reaction conditions: PEHA-1PO (1.0 mmol) in H_2O (5 mL), CO_2 captured (3.3 mmol), C-1 (40 μmol), 2-MeTHF (5 mL), H_2 (80 bar), T = 145 °C, t = 48 h. Yields calculated relative to CO_2 captured as determined by ^{1}H NMR. Calculation error ±5%.

To further validate the proposed reaction sequences and to evaluate the role of amine in the integrated system, a series of experiments were performed. First, we observed that the components of the reaction system including the Ru catalyst and amine can efficiently catalyze the hydrogenation of a gas mixture of $CO_2/3H_2$ to methanol (Fig. 1A). Over 48 h, 24.2 mmol CH_3OH were produced with a TON of 1350 along with 1.4 mmol of formates and 7.1 mmol of formamides. To note, the amount of CH_3OH produced

is around 100% relative to the total amine content in the reaction system. Similar results have been reported previously where the proposed catalytic role of amine could not be established (TON with respect to the amine <2) possibly because of large excess amine being used in most cases [12,20,23,25,27,29,58]. This observation was also raised in a cautionary tale by Barteau et al. [62]. To probe this, CO_2 hydrogenation was carried out with a lower amine loading of 0.8 mmol PEHA (Fig. 1B). Gratifyingly, the reaction pro-

duced 15 mmol of CH_3OH over a prolonged reaction time of 96 h. Relative to the total amino groups present (4.8 mmol), a 313% yield of methanol was achieved ascertaining that *amines turn over* in catalytic CO_2 hydrogenation to CH_3OH. A comparable CH_3OH/amine of 302% was observed by Kayaki and co-workers with a similar catalytic system using linear PEI as the amine [30]. It is also worth pointing out here that the calculated amine TON is essentially an averaged representation of all the amino groups in the system. Although, in the cases of polyamines where the type and chemical nature of all the amino groups are not uniform, the actual TON of an individual N group will vary. Further, while amines can turn over during a hydrogenation reaction, this feature is not relevant to an integrated capture and conversion process where amines are a stoichiometric component of the hydrogenation substrate (ammonium carbamate/bicarbonate).

When the amine and catalyst were physically separated from each other within the reactor (please see experimental section for details), only trace amount of methanol was produced by the catalytic hydrogenation of CO_2, highlighting the cooperative roles of the catalyst and amine in the reaction (Fig. 1C). Similarly, when CO_2-loaded amine was placed in the inner vessel with additional amine and catalyst in the outer vessel, 1.4 mmol of CH_3OH was obtained (Fig. 1D). The CH_3OH obtained in this case is less than 50% of that in the case where no physical compartmentalization exists. This suggest that desorption of the CO_2 captured by amine is possible during the reaction, however it is thermodynamically unfavorable under pressurized conditions. During hydrogenation of CO_2 capture species, formates were observed to be the most abundant C-1 species, apart from CH_3OH. To confirm that such species are intermediates in CO_2-to-CH_3OH reaction, PEHA-formate adduct (formed by reaction of PEHA with HCOOH) was subjected to similar hydrogenation conditions which resulted in an 89% conversion to CH_3OH in 48 h (Fig. 1E).

Finally, the integrated capture and conversion was demonstrated in a biphasic solvent system (Fig. 1G). Previously, our group developed such a system with water and 2-methyl tetrahydrofuran (2-Me-THF) wherein, CO_2 is captured in the aqueous phase containing the amine [41]. Next, the catalyst containing organic (2-Me-THF) phase is introduced and the biphasic system is subjected to hydrogenation. To our advantage, the utilized catalysts are sparingly soluble in water. Hence, following hydrogenation the aqueous layer and organic layer can be easily separated. The formed methanol can be isolated by simple distillation as methanol does not form an azeotrope with water. With CO_2-loaded aqueous PEHA-1PO and Ru-Macho-BH in 2-Me-THF, an overall CH_3OH yield of 82% was achieved upon hydrogenation of the biphasic reaction mixture. The aqueous layer (containing the amine) and organic layer (with the catalyst) can be reused in subsequent cycles.

3. Conclusion

The present study describes an amine assisted integrated carbon capture and utilization (CCU) process to efficiently produce methanol from CO_2. Epoxide-functionalization of PEHA was achieved in an easy, scalable and cost-effective manner leading to formation of amino-alcohol functionalities while increasing the overall molecular weight. The CO_2 capture efficiencies of most of the modified polyamines were found to be significantly high (CO_2/N = 0.50–0.55) and comparable to unmodified PEHA. During hydrogenation of these CO_2-loaded amine solutions, the methanol yields were markedly increased for PO-functionalized PEHA compared to the unmodified counterpart. With modifications in some reaction parameters and using triglyme as the solvent, good to high methanol yields were achieved in most cases, with higher than 90% yields with PEHA-1PO and PEHA-1TFPO.

The role of the amine in CO_2 hydrogenation as well as in an integrated capture and conversion system was validated through a series of control experiments. The highly cooperative role of the catalyst and amine was critical for the hydrogenation to proceed. The hypothesized turnover of amine in CO_2-to-methanol reaction was also ascertained. Furthermore, the integrated system was demonstrated in a biphasic solvent system. In the long term, the present system has potential applications in integration of the already existing CO_2 scrubbing industries with the methanol synthesis plants toward carbon neutral and renewable methanol synthesis.

4. Experimental

4.1. Materials and methods

All experiments were carried out under an inert atmosphere (with N_2 or Ar) using standard Schlenk techniques with the exclusion of moisture unless otherwise stated. Complexes Ru-Macho-BH (**C-1**, Strem Chemicals, 98%), Ru-Macho (**C-2**, Strem Chemicals, 98%) and RuHClPNP^{iPr}(CO) (**C-3**, Strem Chemicals, 98%) were used as received without further purification. All catalysts were weighed inside an argon filled glove box. Tetrahydrofuran (Drisolv, Merck), ethylene glycol (anhydrous, Sigma Aldrich), triglyme (Alfa Aesar), 2-methyltetrahydrofuran (Alfa Aesar) and water (deionized) were sparged with N_2 for 1 h prior to use. Pentaethylenehexamine (technical grade, Sigma Aldrich), propylene oxide (99.5%, Sigma Aldrich), 1,2-epoxybutane (99%, Sigma Aldrich), **(±)**-epichlorohydrin (99%, Sigma Aldrich) and 2-(trifluoromethyl)oxirane (98%, Synquest) were used without further purification. D_2O (CIL, D-99.5%), imidazole (Fischer, 99.5%) and 1,3,5-trimethoxybenzene (99%, Sigma Aldrich) were used as received. ^1H and ^{13}C NMR spectra were recorded on 400, 500 or 600 MHz, Varian NMR spectrometers. ^1H and ^{13}C NMR chemical shifts were determined relative to the residual solvent signals. The gas mixtures were analyzed using a Thermo Finnigan gas chromatograph (column: Supelco, Carboxen 1010 plot, 30 m X 0.53 mm) equipped with a TCD detector (CO detection limit: 0.099 v/v%). CO_2 (Gilmore, instrument grade), 1:3 CO_2:H_2 mix (Airgas, certified standard-spec grade) and H_2 (Gilmore, ultra-high pure grade 5.0) were used without further purification.

Caution: Reactions are associated with H_2 gas. They should be carefully handled inside proper fume hoods without any flame, spark or static electricity sources nearby.

4.2. Preparation of epoxide-functionalized amine in water

The reaction of PEHA with epoxides was carried out following a protocol previously established by our group and others. To a stirred solution of PEHA (2 g) in water (15 mL), the required amount of epoxide was added dropwise at room temperature. The reaction was allowed to stir at room temperature for 24 h. The aqueous solution was used as stock for the required amount in CO_2 capture experiments.

4.3. Standard procedure for CO_2 capture by amine in water

A known amount of amine (PEHA or PEHA-epoxide) was dissolved in water (total volume = 5 mL) in a vial with a magnetic stir bar. The gasses inside the vial were then removed under vacuum. CO_2 was subsequently added while stirring the solution at 800 rpm for 1 h and maintaining the CO_2 pressure inside the reactor at 1 psi above atmospheric pressure. The amounts of CO_2 captured were calculated through gravimetric analysis of the solutions before and after the capture.

4.4. Standard procedure for hydrogenation of CO_2 loaded amine solutions

The capture of CO_2 in aqueous amine solutions were performed prior to hydrogenation reactions. The solution was then purged under N_2 flow to remove any physically absorbed CO_2. In a nitrogen-filled chamber, the CO_2 loaded amine solution, catalyst and co-solvent were added to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. The vessel was then filled with H_2 to the desired pressure (70–80 bar). The reaction mixture was then stirred with a magnetic stirrer for 5 min (800 rpm) and subsequently placed in a preheated aluminum block with stirring at 800 rpm. After heating for a given period, the reactor was cooled to room temperature. The vessel was then cooled in an ice bath for 30 min. Afterwards, the gasses inside the vessel were partly collected in a gas sampling bag for GC analysis whereas the remaining gas was slowly released. Upon opening the reaction vessel, a known amount of internal standard was added to the homogeneous solution which was then analyzed by ^1H and ^{13}C NMR with a deuterated solvent. Yields were determined through ^1H NMR from integration ratios.

4.5. Standard procedure for control studies

In a nitrogen-filled chamber, the catalyst, solvents and substrate (amine, CO_2-loaded amine or amine-formic acid adduct) were added to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. In the case of compartmentalization of the reaction components, a 2 dram borosilicate vial was used as the inner vessel. The vessel was then filled with H_2 or $CO_2/3H_2$ to the desired pressure (70–80 bar). The reaction mixture was then stirred with a magnetic stirrer for 5 min (800 rpm) and subsequently placed in a preheated aluminum block with stirring at 800 rpm. After heating for a given period, the reactor was cooled to room temperature. The vessel was then cooled in an ice bath for 30 min. Afterwards, the gasses inside the vessel were partly collected in a gas sampling bag for GC analysis whereas the remaining gas was slowly released. Upon opening the reaction vessel, a known amount of internal standard was added to the homogeneous solution which was then analysed by ^1H and ^{13}C NMR with a deuterated solvent. Yields were determined through ^1H NMR from integration ratios.

4.6. Standard procedure for CO_2 hydrogenation in a biphasic system

In a nitrogen-filled chamber, the catalyst, 2-Me-THF and aqueous solution of CO_2-loaded amine were added to a 125 mL Monel Parr reactor equipped with a magnetic stir bar, thermocouple and piezoelectric pressure transducer. The vessel was then filled with H_2 to the desired pressure (80 bar). The reaction mixture was then stirred with a magnetic stirrer for 5 min (800 rpm) and subsequently placed in a preheated aluminum block with stirring at 800 rpm. After heating for a given period, the reactor was cooled to room temperature. The vessel was then cooled in an ice bath for 30 min and the gasses inside were slowly released. Upon opening the reaction vessel, a biphasic solution was obtained. The entire solution was transferred to a 15 mL centrifuge tube and the layers were separated carefully. A known amount of TMB was added as internal standard to the organic layer and was then analysed by ^1H and ^{13}C NMR with DMSO–d_6 as deuterated solvent. A known amount of imidazole was added as internal standard to the aqueous layer and was then analysed by ^1H and ^{13}C NMR with D_2O as deuterated solvent. Yields were determined through ^1H NMR from integration ratios.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2022.122331.

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