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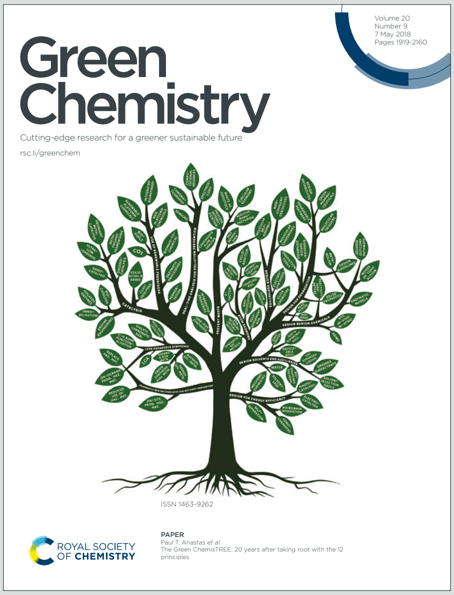

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Towards environmentally benign capture and conversion: Heterogeneous metal catalyzed CO_2 hydrogenation in CO_2 capture solvents.

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Transformation of captured CO_2 into value-added chemicals to mitigate increasing CO_2 concentration in the atmosphere has gained significant attention recently. Though the carbon capture and storage (CCS) is already been practiced in few places, it suffers from energy-intensive CO_2 desorption and compression steps involved, which can be avoided in the carbon capture and utilization (CCU) approach. Herein, a selection of carbon capture solvents were screened to assess the reactivity of condensed-phase heterogeneous metal catalyzed hydrogenation of CO_2. Among catalysts screened, $Cu/ZnO/Al_2O_3$ catalyst was active for the one-pot CO_2 capture and conversion to methanol process using post and pre-combustion carbon capture solvents comprised of various amines and alcohols. Our findings indicate that formamides are less-reactive under our conditions, in comparison to formate ester intermediates noting that a combination of 1° alcohols and amines gives the highest methanol yield. Screening volatile organic compound (VOC)-free alcohols and amines led us to an environmentally benign system of bio-derived and biodegradable chitosan and polyethylene glycol (PEG_{200}), which provide moderate concentration of methanol (139.5 mmol/L) with a facile separation of volatile products (water and methanol). The chitosan/PEG_{200} system was recycled three times, ultimately providing a promising VOC-free, biodegradable, bio-derived and recyclable CO_2 capture and conversion pathway.

1. Introduction

Global CO_2 concentration in the atmosphere has been increasing continuously and this in turn leads to potential environmental issues.[1, 2] The burning of fossil fuels like coal and oil for energy is the primary cause for the continued rise of atmospheric CO_2 level at the rate of 3 ppm each year, recently surpassing 415 ppm in May, 2019.[3] The global demand for energy is steadily increasing and our dependence on fossil fuel for our energy needs has to be subdued as its resources are depleting.[4] In this context, researchers are ramping up their efforts to recycle CO_2 to value added fuels/chemicals.[5-8] The recycling of CO_2 to fuels such as methanol, ethanol, formates etc is shown to be viable upon hydrogenation.[9-11] The hydrogen required for this process can be obtained by water electrolysis using renewable sources such as wind, solar etc. Among the CO_2 hydrogenation products, methanol is a commodity chemical with a global market demand of 78 million tonnes/yr. Methanol is used as a feedstock to produce olefins, fuel blends, acetic acid, formaldehyde and marine fuels.[12]

Various technologies are developed for CO_2 capture;[13] primarily for post combustion CO_2 capture with the aim of being retrofitted to the existing CO_2 sources. Post-combustion CO_2 capture typically involves chemically-selective solvents that are regenerated with thermal heating, where the released and recovered CO_2 can be utilized in a second step as a C_1 source to produce various chemicals.[14] One of the drawbacks with this method is energy intensive CO_2 desorption (ΔH_{abs}=-80 to -85 kJ/mol for 30 wt.% MEA) and compression processes prior to any chemical conversion.[15,16] The thermodynamic penalties associated with the capture process can be lessened when the CO_2 desorption and compression steps are avoided.[17-24] We have previously demonstrated condensed-phase hydrogenation of CO_2 to methanol ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) in the presence of $Cu/ZnO/Al_2O_3$ catalyst in NEt_3/ethanol capture solvent by conceptually bypassing the CO_2 desorption and compression steps.[25] The pre-combustion NEt_3/ethanol capture solvent used in previous studies, while effective, was comprised of low boiling organic liquids, which makes the separation of products (water and methanol) from the capture solvent a challenge. Further, ethanol forms an azeotrope with water and there is high capital and energy costs associated with azeotropic distillation of ethanol and water mixture. As our previous studies had focused on the reactivity of CO_2 captured in pre-combustion (pressure-swing) solvents,[26] we decided to study how the post-combustion (temperature-swing) amines would behave in a similar combined capture and conversion approach.[27,28]

The majority of post-combustion solvents utilize aqueous or non-aqueous formulations of amines and alcohols to capture CO_2, which coincidentally are the same chemical moieties that are used to

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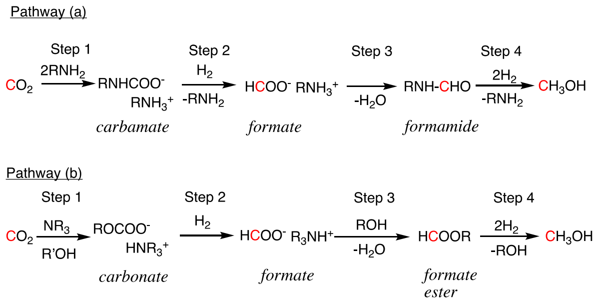
promote catalytic CO_2 hydrogenations.[2, 18, 19, 25, 29] Primary amines capture CO_2 as carbamate species,[30] tertiary amines capture CO_2 only in the presence of water or alcohol and form bicarbonate (HCO_3^-) or alkylcarbonate (RCO_3^-) species.[26, 31] In our approach, the CO_2 hydrogenation to methanol in the condensed-phase can either proceed via formamide (Scheme 1, pathway a) or ester intermediates (Scheme 1, pathway b) in the capture solvent medium. A CO_2 capture solvent typically contains amine or amino alcohol moieties dissolved in aqueous or organic solvents. When primary and secondary amines are used, pathway (a) is favoured, where the formate and formamide intermediates are involved.[2, 32] In the case of tertiary amines, the formate species cannot form formamide as it lacks the -NH- moiety, hence it requires an alcohol group to form ester intermediate, which then gets reduced to methanol (pathway b, Scheme 1).[25, 33]



Scheme 1.

The purpose of the present work is to study the reactivity of CO_2 towards catalytic hydrogenation in both pre-combustion and post-combustion carbon capture solvents, particularly with high boiling capture amines/solvents to improve the productivity and ease the separation of hydrogenation products thereby making the process VOC-free. A second target of this work was to assess bio-derived and biodegradable alcohols and bases to achieve integrated capture and conversion of CO_2 to methanol process as environmentally benign as possible.

2. Experimental

All materials were purchased from commercial suppliers and used without further purification unless otherwise mentioned. Pd/ZnO, Pd/Al_2O_3 and Pd/SiO_2 were prepared by incipient wetness impregnation method.[34] $Pd(NO_3)_2$ and Al_2O_3 were obtained from Engelhard. ZnO and silica gel were purchased from Sigma-Aldrich. $Cu/ZnO/Al_2O_3$ catalyst was obtained from Synetix. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the $Cu/ZnO/Al_2O_3$ showed 55.7 wt.% Cu, 26.8 wt.% Zn, and 5.0 wt.% Al. Catalysts were activated under H_2 atmosphere (50 bar) at 120 °C in a parr reactor (300 mL). After 12h, the remaining H_2 pressure from the reactor was released 120 °C and cooled to room temperature.

Standard procedure for the CO_2 hydrogenation

The above pre-activated catalyst was transferred to a 300 mL Parr reactor and a given amount of amine, alcohol and/or THF were added to the reactor vessel and the reactor was sealed in a nitrogen glovebox. The reactor was first pressurized with CO_2 and then H_2 was introduced. The reactor was heated to set temperature. After 12 or 16 h, the reactor was cooled to room temperature and then to -78 °C, the excess pressure was released slowly. 100 mg of 1,3,5-trimethoxybenzene was added as an internal standard to the reaction mixture (if necessary, DMSO or water was added to the reaction mixture to dissolve the solid). The supernatant was decanted or filtered from the catalyst and analysed by ^1H and ^{13}C NMR experiments.

Recycling experiments

The pre-activated catalyst was transferred to a 300 mL Parr reactor and a given amount of chitosan and alcohol were added to the reactor vessel and the reactor was sealed in a nitrogen glovebox. The reactor was first pressurized with 20 bar CO_2 and then additional 40 bar of H_2 was introduced (total pressure = 60 bar). Then, the reactor was heated to 170 °C. After 12 h, the reactor was cooled to room temperature and then to -78 °C, the excess pressure was released slowly. The insoluble solids (chitosan and catalyst) was separated from the supernatant (alcohol) by centrifugation. 100 mg of 1,3,5-trimethoxybenzene was added as an internal standard to the supernatant and analysed by ^1H and ^{13}C NMR experiments. The solids (chitosan and catalyst) were reused for subsequent cycles. For each cycle, fresh alcohol was added, and above hydrogenation procedure was followed.

3. Results and discussion

Monoethanol amine (MEA)—the most referenced, amine solvent for post-combustion CO_2 capture[35, 36]—was studied as it is less investigated in the literature for combined capture and conversion. MEA was used for the initial screening with the palladium-based heterogeneous catalysts (Table 1). Palladium catalysts were already reported in the literature for N-formylation of amines using CO_2/H_2 in good yields using aliphatic secondary amine substrates. However, compared to the homogeneous catalysts,[37, 38] the heterogenous catalysts have relatively low turnover number (TON <300) for N-formylation.[39, 40] MEA was also attractive from a chemistry standpoint as it contains both primary amine and alcohol moieties that are known to promote the catalytic hydrogenation of CO_2 into methanol via formamide or formate ester intermediates.

At 120 °C, in the presence of a 1 wt% Pd/SiO_2 catalyst, a TON of 255 was obtained for formamide species (**3**) under 55 bar of CO_2:H_2 pressure (TON calculated based on number of moles of product formed per mole of catalyst used and not based on the active sites). THF was used as a solvent as the ethereal or alcoholic solvents were commonly used for hydrogenation studies to improve the catalyst's performance both in homogeneous and heterogenous catalysis.[2, 25, 41] The experiments in Table 1 were studied at higher temperature (>100 °C) as the formation of formamide (**3**) from formate (**2**) typically requires such temperatures in the absence of catalysts. Changing the palladium support from SiO_2 to Al_2O_3 significantly decreased the catalytic activity.

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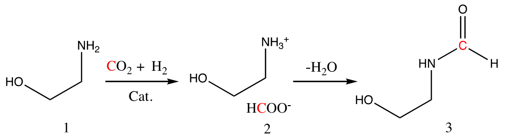
Table 1.

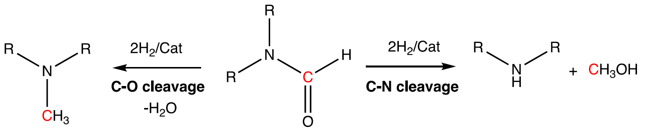


Entry	Catalysts	T (°C)	TON (3)
1	1 wt% Pd/SiO_2	120	255
2	1 wt% Pd/Al_2O_3	120	96
3	1 wt% Pd/SiO_2	150	362
4[a]	5 wt% Pd/ZnO	125	650
5	5 wt% Pd/ZnO	150	1543
6	5 wt% Pd/ZnO	170	693
7[b]	5 wt% Pd/ZnO	150	-

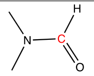
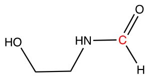
Reaction conditions: catalyst = 30 mg, P = 55 bar (CO_2:1.5 H_2), THF=20 mL, MEA (**1**) = 32.7 mmol, time = 16h, TON was calculated based on ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard. [a]60h, [b]DIPEA (32.7 mmol) was used instead of MEA.

Increasing the temperature from 120 °C to 150 °C increased the TON to 362. The Pd-Zn alloy formed on the reduction of Pd/ZnO was reported to be active towards CO_2 hydrogenation to methanol in gas phase.[42,43,44, 45] In the presence of capture amine, MEA, Pd/ZnO gave a TON of 1543, which is to the best of our knowledge is the highest number reported in the literature for N-formylation. Increasing the temperature further to 170 °C was detrimental to the hydrogenation reaction as it dropped the activity of the catalyst for N-formylation. When a tertiary amine, DIPEA was used as a capture solvent instead of MEA, no detectable amount of any CO_2 hydrogenated products were observed. None of the experiments in Table 1 formed methanol, the final product (or the ester intermediate), therefore we decided to focus on the final step, hydrogenation of formamide.

Table 2.



R = H or alkyl

Entry	Substrates	Catalyst	Hydrogenation product
1		5wt% Pd/ZnO	4% trimethylamine TON = 86
2	 **(3)**	5wt% Pd/ZnO	-

Reaction conditions: catalyst = 30 mg, T=150 °C, P = 55 bar (H_2) entry 1: Dimethylformamide = 32.7 mmol, time=60 h, THF=20 mL; entry 2: **3** = 2.5 mmol, time=16 h, THF=7 mL. TON was calculated based on ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

The hydrogenation of N-formamide can either undergo C-O or C-N bond cleavage.[46] The cleavage of C-N bond of the amide upon hydrogenation form methanol and amine.[2] On the other hand, amide hydrogenation can also proceed via C-O bond cleavage with a liberation of water to form N-methylated amine, which does not form methanol. [47, 48] The selectivity towards the C-N or C-O bond cleavage depends on the catalyst and it is not clearly understood at this point. The hydrogenation of N, N'-dimethylformamide was studied in the presence of Pd/ZnO at 150 °C under 55 bar H_2 pressure (Table 2). It is evident from Table 2, entry 1 that the C-O bond cleavage is favorable in the case of Pd/ZnO catalyst. The hydrogenation of CO_2 in MEA in the presence of $Cu/ZnO/Al_2O_3$ catalyst at 170 °C under 60 bar CO_2/H_2 pressure (CO_2:2H_2), led to mostly decomposition of MEA, and no detectable amount of any CO_2 hydrogenated products were observed by ^1H NMR.

As the catalysts screened in this study towards CO_2 hydrogenation to methanol in MEA led to either decomposition or N-methylation of amine, we turned our attention to other concentrated capture solvents (amines and alcohols). The $Cu/ZnO/Al_2O_3$ is the catalyst of choice as we had shown previously that it is effective for CO_2-to-methanol process in condensed-phase at relatively low temperature, though we knew little of the reactivity of amines and alcohols under these conditions. Several simple alcohols were studied to understand the influence of electronic and steric factors on the formation of methanol through formate ester route (pathway b, Scheme 1).

In Table 3, the effect of alcohol on the CO_2 reduction products were studied. In a neat high boiling amine pre-combustion capture solvent, DIPEA (N,N-diisopropylethylamine, bp. 126.6 °C),[26] in the presence of $Cu/ZnO/Al_2O_3$ without an alcohol at 170 °C, there was a small amount of methanol (19.2 mmol/L) and no detectable amount of formate ester observed by ^1H and ^{13}C NMR experiments. The methanol may have formed from direct hydrogenation of CO_2, in which the CO_2 and H_2 first reacts with Cu and form catalyst surface adsorbed species, HCOO (ad) and H(ad), the well-recognized intermediates.[49-52] Then the polarity effect of DIPEA may have facilitated the reduction of HCOO (ad) species to methanol by lowering its activation barrier.

Upon addition of ethanol to DIPEA, the methanol production has significantly increased to 473.7 mmol/L. This increase is because of the formation of formate ester intermediate, which is known to form under mild condition in the presence of an acidic or basic catalyst. Further reduction of ester in the presence of a catalyst forms methanol, desired product, and ethanol. By changing the alcohol from primary (ethanol) to secondary alcohol (isopropanol or 2-butanol), methanol, ammonium formate and formate ester concentrations decreased with increasing carbon on the alcohol. With *t*-butanol, the methanol and ester concentration decreased significantly to 191.1 mmol/L and no ammonium formate was detected by ^1H NMR. This suggests that the polarity of the solvent is important for the ammonium formate formation (ethanol is more polar than t-butanol) and sterics plays a key role in the formation of ester as the esterification step is known to have affected by the steric hindrance of the alkyl groups on alcohol. ~~Both the polarity and sterics of the solvent affect the formation of methanol and therefore~~ The solvent with high polarity and less steric crowding is favored for this reaction, noting that 1˚ alcohols produced the highest methanol yield under these conditions.

Table 3.

Entry	Capture Solvent	$HCOO^-$ mmol/L	HCOOR mmol/L	CH_3OH mmol/L
1[a]	DIPEA	traces	-	19.2
2	DIPEA-ethanol	72.4	46	473.7
3	DIPEA-isopropanol	32	32	372.3
4	DIPEA-2-butanol	9.2	18.3	330.3
5	DIPEA-t-butanol	0	8.9	191.1

Reaction conditions: $Cu/ZnO/Al_2O_3$=300mg, amine = 20 mmol, alcohol = 200 mmol, time = 16h, P = 60 bar (CO_2:$2H_2$), T = 170 °C, [a]DIPEA = 60 mmol, $HCOO^-$, HCOOR and CH_3OH concentrations were calculated based on ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

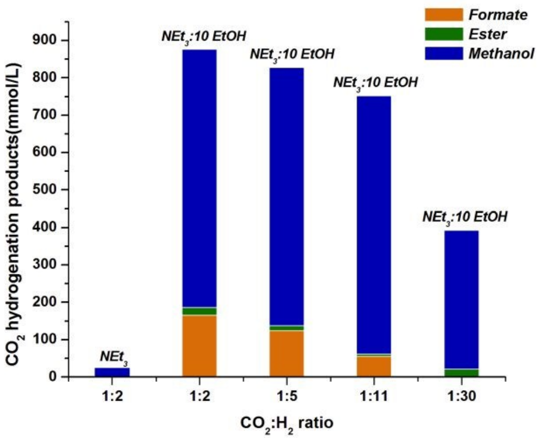


Figure 1. Reaction conditions: $Cu/ZnO/Al_2O_3$=300mg, NEt_3=20 mmol, ethanol=200 mmol, time=12h, T=170 °C, P=60 bar; entry 1, amine=200 mmol; $HCOO^-$, HCOOR and CH_3OH concentrations were calculated based on ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

The change in CO_2/H_2 ratio on the methanol, alkyl ester and ammonium formate concentrations is shown in Figure 1. The NEt_3-ethanol mixture was used instead of DIPEA-ethanol mixture as the less steric NEt_3 gave higher methanol concentration than DIPEA (entry 2, Table 3 vs entry 1, Table 4). Surprisingly, decreasing the CO_2:H_2 ratio from 1:2 to 1:11 did not change the methanol concentration and only the ammonium formate and alkyl ester concentrations decreased. The captured CO_2, carbonates species (step 1, pathway b, Scheme 1) was probably the active species that was getting reduced and thus decrease in CO_2 partial pressure did not change the methanol concentration. In addition, the CO_2 conversion in the case of CO_2:H_2 ratio of 1:2 was 4.7%. The decrease in CO_2:H_2 ratio to 1: 30 increased the CO_2 conversion to 16.1%. However, the total methanol concentration remained the same (689.6 mmol/L), suggesting possible deactivation of the catalyst due to the accumulation of products. Only when the CO_2:H_2 ratio was significantly low (1:30), the methanol concentration decreased to 372.4 mmol/L (CO_2 conversion=21%).

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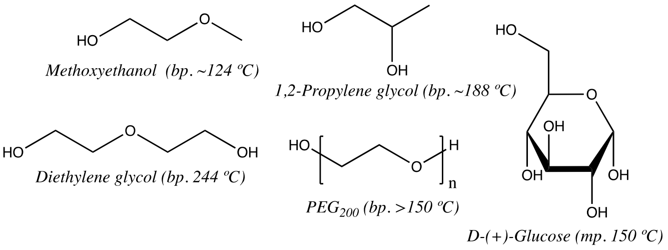
Table 4.



Entry	Capture Solvent	$HCOO^-$ mmol/L	HCOOR mmol/L	CH_3OH mmol/L
1	NEt_3-ethanol	165.5	20.7	689.6
2[a]	NEt_3-ethanol	41.4	124.1	427.6
3	NEt_3-methoxyethanol	107.5	7.5	699
4	NEt_3-1,2-propyleneglycol	traces	traces	950.5
5	NEt_3-PEG_{200}	9.6	traces	490.4
6	NEt_3-diethylene glycol	traces	138.2	975.6
7	NEt_3-glucose	-	-	-

Reaction conditions: $Cu/ZnO/Al_2O_3$=300mg, amine=20 mmol, alcohol=100 or 200 mmol, time=12h, P= 60 bar (CO_2:$2H_2$), T=170 °C; [a]t=110 °C for 6 h and 170 °C for 6 h, $HCOO^-$, HCOOR and CH_3OH concentrations were calculated based on ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

As there are examples, where the formate and ester formed at lower temperatures (~100 °C), we investigated stepwise reduction of CO_2 to methanol by first heating the reaction mixture at 110 °C for 6h and then to 170 °C for 6h to control the catalyst poisoning (entry 2, Table 4). 427.6 mmol/L of methanol was obtained, which is lower than the experiment where the reaction mixture was directly heated to 170 °C for 12h (689.6 mmol/L, entry 1, Table 4). Higher ester concentration in entry 2, Table 4 shows that higher temperature is required to hydrogenate the accumulated ester intermediate to methanol. Higher formate concentration in entry 1, Table 4 demonstrates that the esterification step slows down due to accumulation of water with increasing methanol concentration.

We first assessed the reactivity of varied VOC-free and or environmentally benign 1˚ alcohols under these conditions. Glycols, glymes and polyols have been used as physical solvents for pre-combustion[53] and co-solvents for post-combustion[54-56] CO_2 capture. Further, polyethyleneglycol (PEG) has been shown to be a good medium for metal-catalyzed hydrogenation of CO_2.[57] Among the various high boiling alcohols investigated in Table 4 along with NEt_3, glycols yielded the highest methanol concentrations of 950.5 mmol/L and 975.6 mmol/L (entry 4 and 6, Table 4). Remarkably, the polymer, PEG_{200} also provided high methanol concentration of 490.4 mmol/L which was comparable to ethanol. High boiling properties of glycols and PEG are attractive as the low volatile products, methanol and

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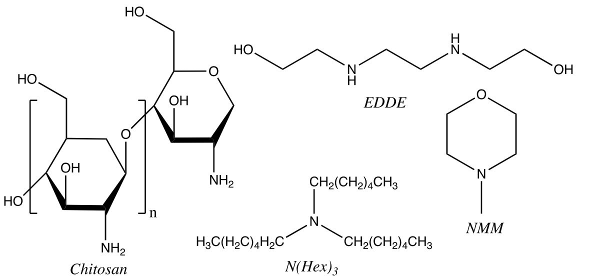
water can be easily separated from these solvents. We note that while diethylene glycol (DEG) had the highest yield of methanol and is VOC-free, DEG is highly toxic and should be avoided. Conversely, the moderate reactivity, low cost and biodegradable nature of PEG makes it attractive alcohol/solvent in a green process.

Glucose was also studied as it is a bio-derived solid alcohol that has four secondary alcohol and one primary alcohol groups in which to react. Glucose was screened for the reaction with NEt_3 as it was expected to behave similar to the simple alcohols that are screened before. Unfortunately, glucose decomposed and charred under our reaction conditions and is unlikely to be viable alcohol source under these conditions.

Table 5.



Entry	Capture Solvent	$HCOO^-$ mmol/L	HCOOR mmol/L	CH_3OH mmol/L
1	NMM-ethanol	-	43.2	446
2	$N(Hex)_3$-ethanol	32.4	54	373
3	EDDE-ethanol	-	299.3[a]	0
4	chitosan-ethanol	-	181.8	227.3
5	chitosan-1,2-propyleneglycol	-	22.7	250
6	chitosan-diethyleneglycol	traces	30	472.7
7	chitosan-PEG_{200}	-	7	139.5

Reaction conditions: $Cu/ZnO/Al_2O_3$=300mg, amine=20 mmol, chitosan=1.5 g, alcohol=100 or 200 mmol, PEG_{200}=20g, time=12h, P=60 bar (CO_2:$2H_2$), T=170 °C, [a]mixture of ester and formamide. $HCOO^-$, HCOOR and CH_3OH concentrations were calculated based on ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

Having the reactivity of high-boiling alcohols, we next studied VOC-free (high boiling) amines/aminoalcohols such as N,N'-Bis(2-hydroxyethyl)ethylenediamine (EDDE), N-methyl morpholine (NMM) and trihexyl amine ($N(Hex)_3$) (Table 5). For the initial studies, the simple alcohol, ethanol was used as a co-solvent since it was previously shown to be compatible with many amines. In NMM and $N(Hex)_3$, methanol concentrations of 446 and 373 mmol/L were obtained, respectively (entry 1 and 2, Table 5). Similar to MEA, use of aminoalcohol, EDDE did not form any methanol, showing that in-situ formed formamide intermediate is difficult to hydrogenate to methanol with the catalysts used in this study.

As with the alcohols, we then focused our efforts to study the reactivity of VOC-free, environmentally benign and biodegradable amines under these conditions. The only amine meeting these criteria is the polysaccharide, chitosan, which is produced by deacylating chitin.[58] Chitosan being the second most abundant natural polymer after cellulose has one primary amine unit and two hydroxyl units. The primary amine group is known to reversibly bind with CO_2 and form ammonium carbamate at room temperature. The D-glucosamine units of chitosan has been shown previously as a CO_2 absorbent by various groups, [59-61] though to our knowledge there have been no studies on using chitosan for CO_2 hydrogenation.

Using chitosan-ethanol mixture as a capture solvent, under our reaction conditions, a moderate methanol concentration of 227.3 mmol/L was obtained. This result is surprising, as chitosan is expected to be a solid under reaction conditions and even more surprising as glucose charred and exhibited zero reactivity. In the case of chitosan, although ester was identified by ^1H NMR, we cannot rule out the possibility of methanol formation via formamide route as chitosan contain primary amine groups. Since ethanol is a volatile alcohol, non-volatile alcohols such as 1,2 propylene glycol, DEG and PEG_{200} were studied under comparable conditions. The chitosan/DEG system showed the highest methanol concentration (472 mmol/L) while 1,2 propylene glycol and PEG_{200} showed moderate methanol formation (250 mmol/L and 139.5 mmol/L respectively).

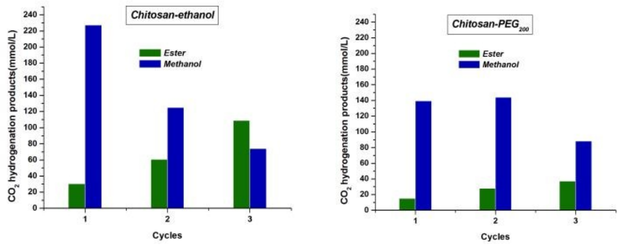


Figure 2. Reaction conditions: $Cu/ZnO/Al_2O_3$=300mg, chitosan=1.5 g, ethanol=200 mmol, PEG_{200}=20g, time=12h, P=60 bar (CO_2:$2H_2$), T=170 °C, $HCOO^-$, HCOOR and CH_3OH concentrations were calculated based on ^1H NMR using 1,3,5-trimethoxy benzene as an internal standard.

After the chitosan reactions, we observed a white solid with particles of catalyst underneath a clear colourless solution that was analysed and shown to contain only ethanol, methanol and water. The built-in separation of solid catalyst and solid amine led us to question whether the base and catalyst could be recovered and reused by decanting the supernatant and introducing fresh alcohol for multiple cycles of hydrogenation of CO_2.

Recycling experiments were attempted with ethanol, DEG and PEG_{200} alcohols. Ethanol recycling experiments showed a decrease in the yield of methanol over multiple cycles (Figure 2a). On the other hand, the concentration of ester continued to increase in subsequent cycles, showing that the catalyst becomes less active for ester hydrogenation. Catalyst sintering could probably be the reason behind the drop in the activity. The accumulation of by-product, water, might have caused the sintering, which was previously observed by us and others in batch reactor experiments.[25, 62]

The recycling experiments with DEG and chitosan showed significant deactivation and the methanol concentration decreased from 472.7 mmol/L in the first cycle to 127.3 mmol/L in the second cycle. There was also obvious leaching of metal into the supernatant

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as it became coloured after the first reaction cycle and therefore the recycling study was stopped after the second cycle.

Interestingly, recycling experiments with PEG_{200} showed no loss in activity in the second cycle, though methanol yield decreased from 139.5 mmol/L to 88.4 mmol/L by the third cycle (Figure 2b). The formate ester concentration increased slightly from the first cycle to the third cycle. The reduced activity in all recycling experiments is indicative of deactivation of the catalyst likely due to sintering, which is expected to be slower in PEG_{200} due to the available charge solvation from the numerous polyether moieties.[63] It is likely that more catalysts that are less susceptible to deactivation would enable a more robust recyclable CO_2 capture and conversion process.

4. Conclusions

In conclusion, we have demonstrated that heterogeneous systems produce methanol via ammonium formate and formate ester intermediate (pathway b, Scheme 1) from CO_2 and capture amine/solvent. Attempts to hydrogenate N-formamide intermediate (pathway a, Scheme 1) to methanol via C-N bond cleavage led to C-O bond cleavage and resulted in N-methylation. Unlike homogenous systems, where both ester and formamide intermediates were known to get hydrogenated further to methanol, heterogeneous system can only hydrogenate ester intermediate to methanol. We have also successfully demonstrated hydrogenation of CO_2 to methanol using capture solvents with high boiling points. Methanol concentration of 139.5 mmol/L was obtained in VOC-free, non-toxic, bio-derived and biodegradable capture solvent medium based on chitosan/PEG_{200}. The chitosan and catalyst were recycled for 3 times with observation of reduced activity after second cycle. The future studies will be focussed on understanding the catalyst deactivation pathway(s) and identifying durable catalyst for the combined CO_2 capture and conversion.

Conflicts of interest

There are no conflicts to declare.

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