Conversion of CO_2 from Air into Methanol Using a Polyamine and a Homogeneous Ruthenium Catalyst

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S *Supporting Information*

ABSTRACT: A highly efficient homogeneous catalyst system for the production of CH_3OH from CO_2 using pentaethylenehexamine and Ru-Macho-BH (**1**) at 125–165 °C in an ethereal solvent has been developed (initial turnover frequency = 70 h^{-1} at 145 °C). Ease of separation of CH_3OH is demonstrated by simple distillation from the reaction mixture. The robustness of the catalytic system was shown by recycling the catalyst over five runs without significant loss of activity (turnover number > 2000). Various sources of CO_2 can be used for this reaction including air, despite its low CO_2 concentration (400 ppm). For the first time, we have demonstrated that CO_2 captured from air can be directly converted to CH_3OH in 79% yield using a homogeneous catalytic system.

Increase in global energy demand fuelled by fossil fuel use has led to a rise in CO_2 concentration in the atmosphere and global warming. Removal of CO_2 from industrial sources or from the atmosphere (carbon capture), together with cutbacks in fossil fuel use, is essential to stabilize and possibly reduce overall CO_2 concentration in the atmosphere. While carbon capture and sequestration (CCS) has been proposed to tackle this problem, another desirable pathway is the carbon capture and recycling (CCR) approach, where CO_2 is recycled back to fuels and materials.[1,2] Many fuel-related C_1 products such as CH_4, CH_3OH, and $HCOOH$ can be obtained by treating CO_2 with H_2. H_2 can be generated by electrolysis of H_2O using renewable energy sources such as solar, wind, etc.[3,4]

Among CO_2 hydrogenation products, CH_3OH is most attractive because it can be directly used as a drop-in liquid fuel for internal combustion engines and direct methanol fuel cells (DMFC). CH_3OH is also a hydrogen storage medium (12.5 wt % H_2) and a convenient chemical feedstock to produce a myriad of chemicals and products including ethylene and propylene (through the MTO process).[5] CH_3OH is already one of the most important building blocks in the chemical industry with an annual production in excess of 70 million tons. Its industrial scale synthesis is based on syngas (CO, H_2, and CO_2) and Cu/ZnO/Al_2O_3-type heterogeneous catalysts under high pressure and elevated temperature (>200 °C).[6] Similar Cu-based heterogeneous catalysts can also use solely CO_2 as a carbon source to produce CH_3OH.[7] Besides heterogeneous catalysts, CH_3OH can be synthesized from CO_2 at mild temperature with metal-based homogeneous catalysts prepared by rational design.[8] In this context, one-pot CO_2 capture and subsequent conversion to fuels

(CCR) has started to attract considerable interest.[9,10] Recently, a Ru-PNP pincer complex was shown to catalyze the hydrogenation of CO_2 to CH_3OH, DMF, and dimethylammonium formate in the presence of Me_2NH and K_3PO_4.[10] Catalyst decomposition was reported at the temperature (155 °C) required to form CH_3OH. Therefore, there is a need for the development of a stable homogeneous catalyst for continuous production of CH_3OH from CO_2.

We report a robust catalyst system for one-pot CO_2 capture and conversion to CH_3OH at relatively mild temperatures (125–165 °C) involving pentaethylenehexamine (PEHA) and a Ru-PNP complex. After CO_2 reduction, CH_3OH can be simply distilled out of the reaction mixture and the system recycled back to make more CH_3OH. Furthermore, for the first time, *CO_2 captured from air is directly converted to CH_3OH*. This is of particular interest in the context of the "methanol economy" aimed at developing an anthropogenic carbon cycle based on recycling CO_2 to CH_3OH using any alternate energy source and modeled on nature's own solar-based photosynthetic carbon cycle. Such a process is already commercially practiced in the George Olah Renewable Methanol plant in Reykjavik, Iceland, using heterogeneous catalysis and geothermal energy.[5a]

Hydrogenation of Gaseous CO_2 to CH_3OH. In homogeneous metal-catalyzed synthesis of CH_3OH through CO_2 reduction, amines are promising materials to capture CO_2 and make it available for further reaction. Amines with a high boiling point and high nitrogen content are preferable to achieve an appreciable CO_2 absorption, i.e., high CO_2/amine and subsequent CH_3OH/amine ratio. They are also preferred for easy separation of the CH_3OH-H_2O mixture after reaction with hydrogen. Polyethylenimines (PEIs) were used extensively for CO_2 capture studies because of their high basicity, high amine content, good thermal stability, and low volatility. However, branched PEIs, linear PEIs, as well as poly(allyl amine) (PAA) have limited solubility in ethereal solvents (THF, 1,4-dioxane, etc.), which are frequently used in homogeneously catalyzed CO_2-to-methanol hydrogenation reactions.[11] A shorter chain polyamine, PEHA, which is soluble in ethereal solvents, was therefore selected for this study. In addition, PEHA is known to have low volatility and good CO_2 capture capacity (from both concentrated CO_2 sources and from air).[12] Employing amines could, however, also have other effects; amines, particularly polyamines, could potentially act as ligands, which may activate (or deactivate) the catalyst.[9a,b,13]

Recently, well-defined pincer metal complexes with N−H functionalities that are known for exhibiting cooperative metal ligand activity were found to be efficient catalysts for hydrogenation and dehydrogenation of many carbonyl functionalities.[14] We speculated that this type of bifunctional pincer metal complexes could also be effective for the production of liquid fuels such as CH_3OH from CO_2 in the presence of amines, which typically involve distinct ammonium carbamate, ammonium formate, and N-formyl intermediates (steps 2−4, Scheme 1). In addition, pincer complexes are known to have high thermal stability and high catalytic selectivity. Using PEHA in THF and 75 bar CO_2/H_2 (1:3), the reaction mixture was heated in the presence of Ru-Macho-BH **1** pincer catalyst and K_3PO_4 first to 95 °C for 18 h and then to 155 °C for another 18 h, as shown in Table 1, entry 1. Sanford and co-workers have described that a "temperature ramp" strategy of heating the reaction mixture first at low temperature and then increasing it to a higher temperature was more favorable than directly heating the catalyst to high temperature because catalyst **1** was reported to decompose at 155 °C.[10] Under our reaction conditions, 9 mmol of CH_3OH (TON = 450) was formed with a CH_3OH/PEHA ratio of 2.6. The presence of PEHA did not seem to deactivate the catalyst. CH_3OH was clearly identified by ^1H NMR (s, 3.3 ppm) and ^{13}C NMR (49 ppm) (Figures S1 and S2). A new formate signal appeared at 8.4 ppm, and a N-formyl signal between 7.8 and 8 ppm (traces) in ^1H NMR. The Ru-Macho complex **2** tested under the same conditions resulted in a TON of 455, comparable to the one obtained with complex **1**. However, the Fe-PNP complex **3**, prepared following a literature procedure,[15] showed no CH_3OH formation by ^1H NMR (Table 1, entry 3). Similarly, use of air-stable Gusev's catalyst **4** failed to produce CH_3OH (Table 1, entry 4).[16] Interestingly, when the −NH moiety of the PNP pincer catalyst **2** was replaced by −NMe in catalyst **5**, no CH_3OH was formed (Table 1, entry 5). This provides evidence of the importance of the −NH moiety in the catalytic cycle, i.e., the involvement of the secondary coordination sphere in the reaction mechanism.[17] However, when catalyst **5** was used, formate and N-formyl intermediates were observed by ^1H and ^{13}C NMR. In our previous work, we showed that when using Ru-PNP pincer complexes, the −NH moiety of the PNP ligand did not have much effect on the formation of the formate salts.[18] However, the −NH moiety of the PNP pincer ligand is important for the formation of CH_3OH from N-formyl intermediates (step 4 in Scheme 1).

In addition to PEHA, we also studied superbases such as DBU (1,8-diazabicycloundec-7-ene) and TMG (1,1,3,3-tetramethyl guanidine) because they are known to capture CO_2[19] and can

Scheme 1. Proposed Reaction Sequence for CO_2 Capture and in Situ Hydrogenation to CH_3OH Using a Polyamine
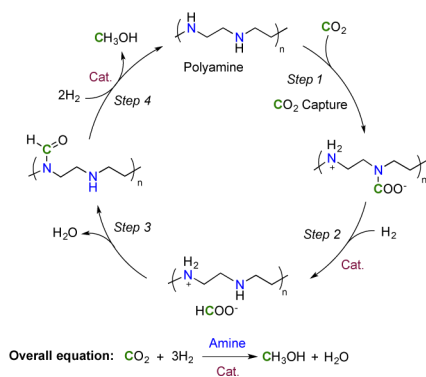

## Table 1. Catalyst Screening for Hydrogenation of CO_2[a]

entry	amine	cat.	T (°C)	additive	CH_3OH[b] (mmol)	TON (CH_3OH)
1	PEHA	1	95−155	K_3PO_4	9	450
2	PEHA	2	95−155	K_3PO_4	9.1	455
3	PEHA	3	95−155	K_3PO_4	–	–
4	PEHA	4	95−155	K_3PO_4	–	–
5	PEHA	5	95−155	K_3PO_4	–	–
6	TMG	1	95−155	K_3PO_4	–	–
7	DBU	1	95−155	K_3PO_4	1.6	80
8	PEHA	1	95	K_3PO_4	–	–
9	PEHA	1	95−155	–	7.6	380
10	–	1	95−155	–	traces	–
11	PEHA	1	155	K_3PO_4	13.8	690
12	PEHA	1	155	–	10.4	520
13	PEHA	1	155	–	21.2	1060

[a]Reaction conditions: PEHA = 3.4 mmol, TMG = 8.5 mmol, DBU = 8.5 mmol, K_3PO_4 = 1 mmol, CO_2/H_2 (1:3) = 75 bar, catalyst = 20 μmol, and THF = 10 mL. Entries 1−7 and 9−10, 95 °C for 18 h and 155 °C for 18 h. Entry 8, 95 °C for 18 h. Entries 11−13, 155 °C for 40 h. [b]Determined by ^1H NMR. TON = turnover number.

efficiently form formate from the captured CO_2.[9a,b] Complex **1**, which was active for CH_3OH formation when used with PEHA, failed to form CH_3OH with TMG, and only formate was observed. With DBU, significantly less CH_3OH was formed (TON = 80). Catalyst **1** was chosen for further studies (although both catalysts **1** and **2** showed similar activity) because of its high activity in hydrogenation studies even under base-free conditions.[14d,e]

When PEHA was heated in the presence of catalyst **1** and K_3PO_4 to 95 °C under 75 bar CO_2/H_2 (1:3), only formate and N-formyl products were observed by ^1H NMR (Table 1, entry 8). A higher temperature was required to form CH_3OH. Interestingly, even in the absence of K_3PO_4, 7.6 mmol of CH_3OH was obtained (Table 1, entry 9). It is commonly accepted that the addition of a base such as K_3PO_4 favors the −NH assisted pathway and thus increases the reactivity of the catalyst in hydrogenation reactions (we also show, vide infra, that the addition of more amine increases CH_3OH formation).[20,17b] In the absence of amine, only a trace amount of CH_3OH was observed (Table 1, entry 10).

Next, to examine the necessity of the temperature ramp strategy, the reaction mixture was directly heated to 155 °C for 40 h in the presence of **1**, PEHA, and K_3PO_4 (Table 1, entry 11). In this case, 13.8 mmol of CH_3OH (TON = 690) was produced with a CH_3OH/PEHA ratio of 4, which shows that catalyst **1** is stable and temperature ramping is not needed. In the absence of K_3PO_4, 10.4 mmol of CH_3OH (TON = 520) was formed (Table 1, entry 12) after 40 h at 155 °C (Figure S3 and S4). Heating the reaction mixture longer (200 h at 155 °C) provided 21.2 mmol of CH_3OH with a TON of 1060 (23% CO_2 conversion to CH_3OH). As shown in Figure 1a, which plots the reaction pressure as a function of time, the hydrogenation of CO_2 was continuous with lower reaction rates toward the end, probably due to the accumulation of products (CH_3OH and H_2O) and/or lower pressure in the reactor.
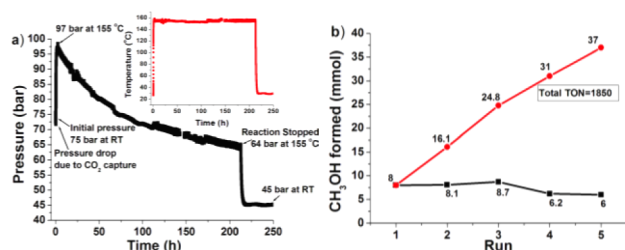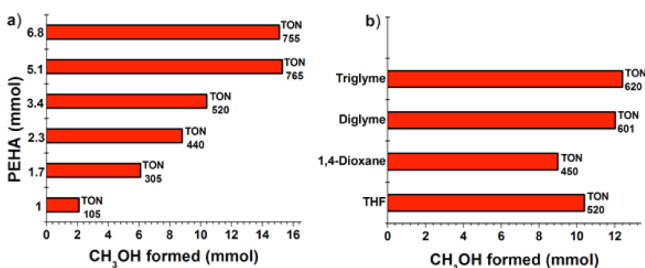
Figure 1. Reaction conditions: PEHA = 3.4 mmol, catalyst 1 = 20 μmol, CO_2/H_2(1:3) = 75 bar, T = 155 °C, and THF = 10 mL. (a) Extended-time study and (b) recycling study (t = 40 h for each run). Black line, CH_3OH formed in each run; red line, total amount of CH_3OH formed. CH_3OH amount was determined by ^1H NMR.

The recyclability of catalyst 1 was studied using PEHA in THF and 75 bar CO_2/H_2 (1:3) (Figure 1b). The same catalyst was reused for 5 consecutive CO_2-to-CH_3OH hydrogenation cycles. The CH_3OH and H_2O formed in the reaction were distilled out of the solution along with THF at the end of each cycle. More than 75% of the initial activity was retained after 5 cycles, and a total TON of 1850 was reached.

Having tested the robustness and recyclability of the catalyst, we decided to focus on increasing the CH_3OH yield. First, the effect of amine content on CH_3OH formation was investigated by varying the amine content from 1 to 6.8 mmol under 75 bar CO_2/H_2 (1:3). The CH_3OH yield increased with rising amine concentration as shown in Figure 2a; 5.1 mmol of PEHA seemed to be the optimum amine concentration to obtain the highest TON of 765. Increasing further the amine amount from 5.1 to 6.8 mmol did not result in a higher TON for CH_3OH formation.

Because the boiling point of THF (66 °C) and CH_3OH (64.7 °C) are very close, we decided to screen higher boiling ethereal solvents such as 1,4-dioxane (101 °C), diglyme (162 °C), and triglyme (216 °C) to facilitate the separation of CH_3OH-H_2O after reaction. Diglyme and triglyme gave higher CH_3OH TONs than THF or 1,4-dioxane (Figure 2b). Unlike in heterogeneous catalysis studies, few homogeneous metal-catalyzed CO_2 hydrogenations discuss the CO concentration in the gas mixture.[21] In the analysis of the gas mixture after each reaction, vide supra, 0.2–0.4% CO was generally observed. Using a heterogeneous catalyst, Urakawa and Bansode showed that by decreasing the CO_2/H_2 ratio, the CO content in the gas mixture could be reduced.[21] Similarly, in our system, we observed that by decreasing the CO_2/H_2 ratio from 1:3 to 1:9, the CO concentration can be reduced to 0.1% from 0.4% under the same pressure (75 bar). In addition, using a 1:9 ratio of CO_2/H_2, the CH_3OH yield (based on CO_2)

Figure 2. Effect of (a) PEHA content and (b) solvent on the CH_3OH formation. Reaction conditions: catalyst 1 = 20 μmol, CO_2/H_2(1:3) = 75 bar, T = 155 °C, t = 40 h, and solvent = 10 mL. In the case of (a), THF and (b), 3.4 mmol PEHA were used. CH_3OH amount was determined by ^1H NMR.

increased from 13% (TON = 620) to 27% (TON = 500) (Figure S5a). The effect of temperature on CH_3OH formation and CO content was studied with catalyst 1 under 75 bar CO_2/H_2 (1:3) (Figure S5b). When the temperature was lowered from 165 to 125 °C, the CO concentration in the gas mixture decreased from 0.6% to 0.1%. At 145 °C in particular, high CH_3OH (TON = 600) and low CO (0.2%) content were observed.

Therefore, by lowering the reaction temperature and decreasing the CO_2/H_2 ratio, CO content in the gas mixture can be reduced. Under optimized conditions, at 145 °C, a CH_3OH yield as high as 65% was obtained (with an initial turnover frequency of 70 h^{-1} in the first hour), whereas at 125 °C, 54% yield was obtained (Table 2). To our delight, no detectable amount of CO was observed by gas chromatography (GC) analysis of the gas mixture (CO detection limit: 0.099 v/v%) at either 125 or 145 °C. However, by Fourier transform infrared (FTIR) analysis, traces of CO were detected. Recycling studies in triglyme were performed under 75 bar CO_2/H_2 (1:9) at 145 °C. CH_3OH and H_2O were distilled out from the reaction mixture after each hydrogenation cycle. The PEHA, catalyst, and triglyme were reused for subsequent runs. A cumulative TON of 2150 was obtained after five runs, and the catalyst was still active with 75% of the initial activity (Figure S6). When the reaction was scaled-up 4-fold, 98 mmol (4 mL) of methanol was obtained, and the required CO_2/H_2 was refilled repeatedly at constant pressure (Figure S7). The resting states of the catalyst were also studied by NMR and Electrospray ionization mass spectrometry (see SI).

CO_2 Capture from Air and Conversion to CH_3OH. CO_2 capture from air was performed by bubbling air (synthetic air, 400 ppm of CO_2 in N_2/O_2 80/20) in an aqueous solution of PEHA at a flow rate of 200 mL/min for 64 h (Scheme 2, Table 3). Analyses of the mixture after CO_2 capture showed carbamate and bicarbonate/carbonate signals between 161 and 165 ppm in ^{13}C NMR. Integration of this region with respect to the aliphatic region corresponded to 5.4 mmol of CO_2 captured from air by 3.4 mmol of PEHA in ^{13}C NMR (Figure S12). With catalyst 1 at 155 °C, when using 1,4-dioxane/H_2O and triglyme/H_2O mixtures as solvents under 50 bar H_2 pressure, 2.1 (39% yield) and 3.3 (61% yield) mmol of CH_3OH (Figure S13) were obtained, respectively, from the atmospheric CO_2 in the PEHA solution. When the reaction mixture was heated longer, 79% CH_3OH yield was achieved. Six percent of the captured CO_2 was converted to formate, and the remaining 15% probably remained unreacted as carbamate and bicarbonate/carbonate mixture (observed in the ^{13}C NMR). GC and FTIR analysis of gas mixtures after the reactions showed no detectable amount of CO.

In conclusion, we have developed for the first time a highly efficient homogeneous Ru-based catalyst for the production of CH_3OH from CO_2 and H_2 using a polyamine at 125–165 °C in an ethereal solvent. The CH_3OH/H_2O obtained were separated by simple distillation, and the catalyst, solvent, and amine were reused in subsequent CO_2-to-CH_3OH reaction cycles. Furthermore, to the best of our knowledge, we present here the first

Table 2. Extended-Time Study at 145 and 125 °C[a]

entry	CO_2/H_2	T (°C)	CH_3OH (mmol)	TON (CH_3OH)	NMR yield (%)
1	1:9 (75 bar)	145	24	1200	65
2	1:9 (75 bar)	125	19.7	985	54

[a]Reaction conditions: PEHA = 5.1 mmol, catalyst **1** = 20 μmol, CO_2/H_2 (1:9) = 75 bar, t = 200 h, and triglyme = 10 mL.

Scheme 2. CO$_2$ Capture from Air and Conversion to CH$_3$OH
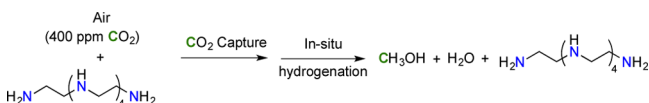
Table 3. CO$_2$ Capture from Air and Conversion to CH$_3$OH^a

entry	amine	CO$_2$ captured (mmol)	solvent	CH$_3$OH (mmol)	NMR yield (%)
1	PEHA	5.4	1,4-dioxane	2.1	39
2	PEHA	5.4	triglyme	3.3	61
3^b	PEHA	5.4	triglyme	4.3	79

^{a}Reaction conditions: PEHA = 3.4 mmol, catalyst **1** = 20 μmol, H$_2$ = 50 bar, t = 40 h, T = 155 °C, and organic solvent (10 mL)−H$_2$O (8 mL). $^b t$ = 55 h.

example of CO$_2$ capture from air and direct conversion to methanol with a homogeneous catalyst. Up to 79% of the CO$_2$ captured from air was converted to CH$_3$OH. By implementing our method in a flow system, continuous production of CH$_3$OH can be achieved.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12354.

Additional experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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