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Introduction

Carbon capture and sequestration (CCS) is being explored as a potential option to mitigate CO₂ accumulation.¹ Unfortunately, extensive energy input into the desorption/compression process is a crucial barrier to realize practical CCS. On the other hand, as a nontoxic, abundant, renewable C1 building block, catalytic transformation of CO₂ would be promising for the production of fuels and value-added chemicals.² However, the reactions involving CO₂ are commonly carried out at high pressure, which may not be economically suitable and also poses safety concerns. In this context, we have proposed carbon capture and utilization (CCU) for the formation of useful chemicals as an alternative approach to addressing the energy penalty problem in CCS.³ Moreover, CO₂ reduction as a utilization approach could be an option for energy storage.⁴ Recently, Olah and co-workers have initiated a methanol economy strategy for supplying renewable energy in a carbon neutral cycle.5

Hydrogenation of CO_2 to formic acid and its derivatives has been appealing for suitable liquid hydrogen sources due to easy storage and transportation.⁶ The presence of a base is

In situ hydrogenation of captured CO₂ to formate with polyethyleneimine and Rh/monophosphine system[†]

Yu-Nong Li, Liang-Nian He,* An-Hua Liu, Xian-Dong Lang, Zhen-Zhen Yang, Bing Yu and Chao-Ran Luan

 CO_2 in the air can be efficiently captured with simultaneous activation by PEI (polyethyleneimine) to form ammonium carbamate and/or carbonate species. Thus, the *in situ* hydrogenation of captured CO_2 into energy-storage materials rather than going through the desorption of conventional CCS (carbon capture and storage) runs better in comparison with equivalent gaseous CO_2 , thus validating this potential application of CCU (carbon capture and utilization) for supplying renewable energy. PEI_{600} as an effective carbon absorbent in this study could also be assumed to serve as both ligand and base to promote the catalytic hydrogenation of captured CO_2 , consequently acting as a 'hinge base' to combine capture and hydrogenation processes. The pathway was studied by NMR and *in situ* FT-IR spectroscopy under CO_2 pressure. This protocol could open up great potential in transforming the captured CO_2 from waste to fuel-related products.

required to overcome the thermodynamic limitation. In this aspect, inorganic bases are often used for aqueous systems.⁷ Nitrogen-containing bases like $NH(CH_3)_2$, trialkylamines,⁸ imidazoles, quinolines,⁹ and amino-functionalized ionic liquids,¹⁰ commonly work well and lead to the formation of a "base–formic acid" adduct, or formate, or formamide.¹¹ In addition, CO₂ hydrogenation is usually performed at high CO₂ pressure and temperature.

We envisage that the utilization of PEI, e.g. PEI_{600} (M_w = 600 Da, Scheme S1, see ESI⁺), for CO₂ hydrogenation could be more attractive due to its strong basicity, non-volatility and good stability. In particular, PEI is proved to be an excellent CCS absorbent which can absorb CO₂ directly from the air. Notably, three types of amines (i.e. primary, secondary and tertiary amine) could improve capture efficiency.¹² Notably, the amino group in the repeating unit may also serve as a ligand to alter the reactivity of the transition metal catalyst. Furthermore, captured CO₂ as an activated species is more easily converted to value-added chemicals via forming C-O/C-N bond.^{3a-c} Herein, we would like to validate the strategy of CO₂ capture with simultaneous activation and in situ hydrogenation of the captured CO₂ to produce fuel-related products such as formic acid derivatives by the combined PEI₆₀₀ with RhCl₃·3H₂O/CyPPh₂ system.

Results and discussion

 CO_2 is supposed to be absorbed by PEI_{600} via the formation of the ammonium carbamate 1 (Scheme 1a).¹² On the other

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State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, People's Republic of China. E-mail: heln@nankai.edu.cn;

Fax: (+86)-22-2350-3878; Tel: (+86)-22-2350-3878

[†]Electronic supplementary information (ESI) available: General experimental methods, experimental procedures and results, characterization for absorption and hydrogenation systems, and copies of NMR, *in situ* FTIR, GC-MS spectra. See DOI: 10.1039/c3gc41265b



Scheme 1 CO₂ capture with PEI.

hand, the ammonium alkylcarbonate 2 pathway could also be preferential in the presence of alcohol (Scheme 1b).⁹ The capture mechanism is further investigated by *in situ* FT-IR under CO₂ pressure and NMR techniques.

In the ¹³C NMR spectrum of CO₂ capture by PEI₆₀₀ in methanol, additional signals at 164.01 and 159.51 ppm can be assigned to C=O bands in ammonium carbamate **1** and ammonium methylcarbonate **2** (R = Me), respectively (Fig. S1, see ESI[†]).

Likewise, an upfield shift of carbons in PEI_{600} is observed upon CO₂ sorption. *In situ* FT-IR shows that the C==O stretching vibration of the ammonium carbamate at 1705, 1694, 1676 cm⁻¹ gradually increases upon CO₂ uptake (Fig. S2, ESI†). N-H asymmetric and symmetric deformation bands at 1592–1586, 1552–1523 cm⁻¹, and N-H bending vibration of NHCOO⁻ at 1496 cm⁻¹ suggest the formation of the carbamate 1. The characteristic peak of C==O in ammonium methylcarbonate 2 at 1570 cm⁻¹ presumably supports path *b*. Finally, because of the lack of a band at 835 cm⁻¹, we could exclude the formation of bicarbonate anion.¹³

Subsequently, hydrogenation of gaseous CO₂ was initiated by employing a concise and well-documented RhCl₃·3H₂O/ PPh3/base catalytic system in methanol. PEI600 showed excellent performance at 60 °C, better than typical bases^{9,14} used in previous reports,15 including primary amine (monoethanolamine), secondary amine (diethanolamine, Et₂NH and morpholine), tertiary amine (triethanolamine, DABCO (triethylenediamine), TMEDA (N,N,N',N'-tetramethylethylenediamine), HMTA (hexamethylenetetramine)), quaternary ammonium salt (^{*n*}Bu₄Br) and inorganic base *e.g.* KOH (Table 1, entry 1 ν s. entries 2-11). Accordingly, base strength and solubility limitation could have an impact on the reaction outcome.9 Moreover, increasing the reaction temperature would cause the catalytic activity to sharply drop (entries 1, 12, 13), whereas the temperature below 40 °C also gave an inferior result (entry 14 vs. 1). That is probably because hydrogenation of CO_2 to HCOOH is an exothermic reaction,¹⁶ thus, increasing temperature is not beneficial to the reaction. Meanwhile, higher temperature could also be detrimental to PEI600 and the catalyst system leading to more side reactions at the expense of product selectivity. Hence, when the temperature was increased to 60 and 100 °C, the yields sharply dropped. On the other hand, higher temperature could facilitate the reaction. Therefore proper temperature is needed to run the reaction. Indeed, 40 °C gave an inferior result and 60 °C showed the best result.

Table 1 Hydrogenation of gaseous CO₂ by RhCl₃·3H₂O/PPh₃^a

Entry	Base	pK_a of the conjugated acid ^d	T (°C)	TON ^b
1 ^{<i>c</i>}	PEI600	$\sim 10^{e}$	60	465
2	MEA	9.50^{f}	60	35
3	DEA	$7.77 - 9.50^{f}$	60	123
4	Et_2NH	10.98^{f}	60	107
5	Morpholine	8.36 ^{<i>f</i>}	60	220
6	TEA	7.77 ^{<i>f</i>}	60	207
7	TMEDA	9.42^{g}	60	109
8	DABCO	8.72^{g}	60	310
9	HMTA	4.89 ^g	60	62
10	ⁿ Bu ₄ Br	$13^{h}, -9^{i}$	60	n.d.
11	KOH	$(31.2)^{j}$	60	21
12^{c}	PEI600		100	n.d.
13 ^c	PEI ₆₀₀		80	103
14^c	PEI ₆₀₀		40	222

^{*a*} Conditions: RhCl₃·3H₂O (0.01 mmol, 2.6 mg), PPh₃ (0.1 mmol, 26 mg), base (3.5 mmol), methanol (3 mL), CO₂ (4 MPa), H₂ (4 MPa), 16 h. ^{*b*} Refers to HCOO⁻BH⁺, determined by ¹H NMR using 1,1,2,2-tetrachloromethane as internal standard, TON = turnover number: moles of formate per mole of Rh catalyst. ^{*c*} PEI₆₀₀ (0.5 mmol, 0.3 g). ^{*d*} pK_a values in water, and values in DMSO are given in brackets. ^{*e*} Ref. 14*a*. ^{*f*} Ref. 14*b*. ^{*g*} Ref. 14*a*. ^{*h*} Ref. 14*a*. ^{*i*} Ref. 9.

Table 2 Screening phosphine ligands^a

Entry Ligand TON ^b Entry Ligand	
	TON ⁴
1 ^c — 7 14	24
2 PPh_3 465	
$3 P^n B u_3$ 138 BINAP	
4 PCy ₃ 32 15 ^{Ph}	13
5 $(2-Furyl)_3P$ 0 $Ph_2P^{-P}Ph_2$	
6 PPhEt ₂ 447 Pentaphenyl triphosphan	
7 PPhCy ₂ 80 16	108
8 $(o-\mathrm{Tolyl})\mathrm{PPh}_2$ 24	
9 (p-Tolyl)PPh ₂ 398 Pyphos PPh ₂	
10 PPh ₂ Cy 481 17	n.d.
11^c PPh ₂ Cy 542	
12 ^{<i>c,d</i>} PPh ₂ Cy 852 P ^{<i>t</i>} Bu ₂ V 'BuDavePhos	
13 $\stackrel{\text{'Pr}}{\underset{\text{'Pr}}{\bigvee}}$ n.d. 18 $\underset{\text{terPy}}{\bigvee}$ $\underset{\text{terPy}}{\bigwedge}$	14

^{*a*} Conditions: RhCl₃·3H₂O (0.01 mmol, 2.6 mg), ligand (0.1 mmol), PEI₆₀₀ (0.3 g), methanol (3 mL), CO₂ (4 MPa), H₂ (4 MPa), 60 °C, 16 h. ^{*b*} Refers to HCOO⁻BH⁺, determined by ¹H NMR. Formic acid was separated by distillation and the characterization charts are given in the ESI.[†] ^c RhCl₃·3H₂O (0.005 mmol, 1.3 mg), ligand (0.05 mmol, 13 mg). ^{*d*} 32 h.

The results stimulated us to further study the phosphine ligand effect. CO_2 hydrogenation almost did not occur in the absence of phosphine ligand (entry 1, Table 2). Electron-donating phosphine ligands were firstly screened because they could favor the *in situ* formation of the catalytic species.¹⁷ In this study, PPh₃ gave a better result than P^{*n*}Bu₃, PCy₃, (2-furyl)₃P (entry 2 *vs.* entries 3–5). CyPPh₂ showed the highest activity among the alkylphenylphosphines, tentatively being attributed

to its appropriate steric and electric effect (entry 10 vs. entries 6–9). To our delight, a TON of up to 852 can be obtained through roughly optimizing the reaction conditions (entries 11–12). The sterically hindered ligand ^{*t*}Bu-XPhos was inactive (entry 13), while other bidentate and multidentate ligands such as BINAP, pentaphenyltriphosphan, pyphos, ^{*t*}BuDavePhos, and terPy exhibited inferior activity in comparison with the monodentate ligands (entries 14–18). This is presumably because the structural flexibility of less hindered monophosphines could facilitate the ligand exchange to offer free sites for coordination with metal. In addition, other metal salts were also examined with PEI₆₀₀/CyPPh₂/methanol system. RhCl₃·3H₂O gave the best results among RuCl₃·6H₂O, PdCl₂, Rh(acac)₃, NiCl₂·6H₂O and Fe(BF₄)₂·6H₂O (Table S1, ESI[†]).

We next investigated hydrogenation of the captured CO_2 using $PEI_{600}/RhCl_3 \cdot 3H_2O/CyPPh_2$ system with non-volatile ethylene glycol as a solvent. PEI_{600} in ethylene glycol can absorb gaseous CO_2 smoothly to afford the PEI-CO₂ adducts *i.e.* **1** and **2** (Scheme 1) with a capacity of 0.159 g $CO_2/0.3$ g PEI_{600} . Then, the hydrogenation reaction proceeded with the absorbed mixture after the consecutive introduction of $RhCl_3 \cdot 3H_2O$, $CyPPh_2$ and hydrogen. Formate with regard to the $PEI-CO_2$ adduct was obtained in 37% yield (Table 3, entry 1). To the best of our knowledge, this is the first example of the *in situ* hydrogenation of captured CO_2 into an energy-storage material rather than going through the desorption step of conventional CCS.

Table 3	Hydrogenation	of the	captured CC) ₂ ^a
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Entry	Substrate	Captured CO ₂ (mmol)	TON^{b}	Yield (%)
1^d	PEI ₆₀₀ -CO ₂ /glycol	3.6	260	37
2 ^e	H_2^{+} N_{-}^{+} N_{-}^{-} N_{-}^{-} N_{-}^{-}	5.6	126	12
3^f	$H_2N \sim N \sim$	9.7	291	15
4^g	$ \underbrace{ \begin{pmatrix} N, \\ + \\ N \\ H \end{pmatrix}}_{H} \stackrel{O}{=} \underbrace{ \begin{pmatrix} O \\ O \\ - \\ O \\ 3 \end{pmatrix}}_{H} $	5.5	117	11
5 ^{<i>h</i>}	HO O O	5.5	500	46
6 ^{<i>i</i>}	HO O O	6.6	726	55
7 ^j	HCO ₃ .	0.6	22	19
8 ^k	CO_2 (gas)	3.6	168	23

^{*a*} Conditions: RhCl₃·3H₂O (0.005 mmol, 1.3 mg), CyPPh₂ (0.05 mmol, 13 mg), methanol (2 mL), H₂ (4 MPa), 60 °C, 16 h. ^{*b*} Refers to HCOO⁻BH⁺, determined by ¹H NMR. ^{*c*} Relative to the amount of captured CO₂. ^{*d*} PEI₆₀₀ (0.5 mmol)/glycol (18 mmol). ^{*e*} DETA (2.9 mmol)/glycol (18 mmol). ^{*f*} DEN (5 mmol)/glycol (31 mmol). ^{*g*} DBN (5 mmol)/triethylene glycol (6 mmol). ^{3*a*} ^{*h*} DBN (5 mmol)/glycol (6 mmol). ^{*i*} DBN (5 mmol)/glycol (5/ 56 mmol). ^{*k*} CO₂ (3.6 mmol, 0.2 MPa) with fresh PEI₆₀₀ (0.5 mmol, 0.3 g), glycol (18 mmol, 1 mL).

Furthermore, direct hydrogenation of several ammonium carbamates derived from CO_2 , e.g. DETA⁺CO₂⁻ (DETA = diethylenetriamine), ammonium carbonates such as [DBNH] $[OCO_2(C_2H_4O)_3H]$, [DBNH] $[OCO_2CH_2OH]$ (DBN = 1,5-diaza bicycle[4.3.0]non-5-ene), was also successfully performed (entries 2-6, Table 3). It is worth mentioning that a TON of 726 can be attained (entry 6). To a certain extent, increasing the amount of the absorbent and the base gave better results (entry 3 vs. 2, 6 vs. 5). On the other hand, the ammonium carbonate showed a slightly higher activity than the ammonium carbamate by using an equal amount of absorbent (entry 5 vs. 3, Table 3). In addition, aniline bicarbonate can somehow be hydrogenated under the present conditions although there is solubility limitation (entry 7). Notably, the captured CO_2 can facilitate the hydrogenation and thus gave a higher reaction rate and better results (entry 8 vs. 1) in comparison with equivalent free gaseous CO₂, probably implying CO₂ activation upon capture with PEI (Fig. S4, ESI⁺).

In situ FT-IR under CO_2 pressure and NMR study were performed to gain deeper insight into the one-pot process for CO_2 capture and subsequent hydrogenation of the captured CO_2 . The appearance of the carbonyl peak at 1676 cm⁻¹ supports the formation of ammonium carbamate upon uptaking CO_2 (Fig. 1). Intensity changes at 1950, 2000–2079 cm⁻¹, and characteristic peaks at 1579 and 1353 cm⁻¹ suggest the generation of the formato-Rh complex during the hydrogenation step. Broad absorptions from 1776 to 1810 cm⁻¹ could be suggestive of formic acid and derivatives, indicating the target product formation.¹⁸

Furthermore, the ¹H NMR spectrum also exhibits characteristic signals¹⁹ of Rh–H species at -17.76 (d, $J_{\text{Rh-H}} = 108$ Hz) and -19.18 ppm (d, $J_{\text{Rh-H}} = 92$ Hz) (Fig. 2). The cyclohexyl protons shift upfield upon the addition of PEI₆₀₀, illustrating that PEI₆₀₀ could weaken the coordination between Rh and CyPPh₂ (Fig. S5, ESI[†]). ³¹P NMR study implies ligand exchange of phosphine with PEI₆₀₀ (Fig. S6, ESI[†]). Furthermore, N–H peaks in *in situ* FT-IR move to the lower frequency region upon



Fig. 1 Monitoring of the reaction process by *in situ* FT-IR under CO₂ pressure. Conditions: RhCl₃-3H₂O (0.03 mmol, 7.9 mg), CyPPh₂ (0.3 mmol, 80 mg), PEI₆₀₀ (1.5 mmol, 0.9 g), methanol (9 mL), H₂ (4 MPa), CO₂ (4 MPa), 60 °C, 13 h. The spectrum of PEI₆₀₀ was subtracted. 2340 cm⁻¹ can be assigned to the gaseous CO₂ peak.



Fig. 2 ¹H NMR spectrum of the reaction mixture showing the formation of the Rh–H species (400 MHz, CDCl₃). Reaction conditions: RhCl₃·3H₂O (0.01 mmol, 2.6 mg), CyPPh₂ (0.1 mmol, 26 mg), PEl₆₀₀ (0.5 mmol, 0.3 g), methanol (2 mL), H₂ (4 MPa), CO₂ (4 MPa), 60 °C.



Fig. 3 In situ FT-IR spectrum of the mixture in the absence of CO_2 and hydrogen. Conditions: RhCl₃·3H₂O (0.02 mmol, 5.2 mg), CyPPh₂ (0.2 mmol, 53 mg), PEl₆₀₀ (1 mmol, 0.6 g), methanol (6 mL), 1.5 h. The spectrum of the mixture of CyPPh₂ and CH₃OH was subtracted. Peaks **a** and **b** correspond to the stretching and bending vibrations of N–H, respectively.

the introduction of $RhCl_3 \cdot 3H_2O$, indicating the possible coordination of PEI_{600} with Rh (Fig. 3).²⁰

Based on the experimental results in this study and recent reports²¹ on the hydrogenation of CO_2 derivatives including carbamates, carbonates, ureas, and amides, the proposed pathway for the combined process of carbon capture with *in situ* hydrogenation is shown in Scheme 2. Although gaseous CO_2 can be hydrogenated to formic acid *via* a well documental mechanism, the present process likely proceeds through initial capture and subsequent hydrogenation of the captured species, *i.e.* ammonium carbamate **1** and ammonium methylcarbonate **2**. Decoordination of PEI from Rh–hydride species **3** *in situ* formed from RhCl₃, phosphine and PEI, could provide two free sites for the coordination of **1** or **2** with Rh leading to



Scheme 2 Proposed pathways of carbon capture and subsequent hydrogenation of the captured CO_2 .

the formation of the intermediate $[Rh(\eta^2-OCHO)]$ **4**. The intraproton transfer along with the cleavage of the C–N or C–O bond, and subsequent hydride transfer to the carbonyl group could result in the formation of complex 5. Finally, oxidative addition of H₂ to complex 5 gives the dihydride intermediate **6**, and HCOO⁻BH⁺ is produced *via* reductive elimination with regenerating the Rh–hydride species 3 to complete the catalytic cycle.

Conclusions

In summary, the present PEI/RhCl₃·3H₂O/CyPPh₂ sequential protocol provides a successful example for CO₂ capture and subsequent hydrogenation of the absorbed CO₂, validating the CCU strategy to supply energy products as a part of a carbon neutral cycle. CO₂ is likely captured by PEI to form the carbamate and/or carbonate species, which can sequentially be hydrogenated to formate. The reaction was studied by NMR and *in situ* FT-IR spectroscopy under CO₂ pressure. This process could avoid energy input for the desorption step, and could open up great potential for transforming the captured CO₂ from waste to fuel-related products.

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