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## Condensed-Phase Low Temperature Heterogeneous Hydrogenation of CO<sub>2</sub> to Methanol

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A low-temperature  $CH_3OH$  synthesis was achieved at 120-170 °C using tertiary amine and alcohol in the presence of  $Cu/ZnO/Al_2O_3$  catalyst by  $CO_2$  hydrogenation. A series of 1°, 2° and 3° amines and alcohols were screened to study its influence on the formation of  $CH_3OH$ . Particularly, 3° amines such as NEt<sub>3</sub> in combination with EtOH formed  $CH_3OH$  with 100% yield with respect to the amine. Unlike the traditional gas-phase heterogeneous metal catalyzed  $CO_2$ -to- $CH_3OH$  reactions, no CO is used in the feed gas mixture in this method. In addition, the hydrogenation gives good selectivity (>95%) for  $CH_3OH$  and only trace amounts of CO and  $CH_4$  are formed. The presence of CO in the gas mixture was attributed to the decomposition of  $CH_3OH$  product, which was confirmed by high-temperature and high-pressure MAS NMR. The reaction was performed in the condensed phase at relatively lower temperature, thus the RWGS reaction, which typically operates at >250 °C, was significantly reduced at this temperature (120-170 °C). The first *in situ* spectroscopic evidence for the condensed phase hydrogenation of alkylcarbonate to  $CH_3OH$  via ammonium formate and alkylformate intermediates was also presented under the experimental conditions.

### Introduction

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Anthropogenic  $CO_2$  emissions into the atmosphere are increasing continuously and it has been widely accepted as a primary cause of global warming and climate change.<sup>1</sup> Similar to the nature's photosynthesis, where the CO<sub>2</sub> is used to construct complex carbon frameworks to store energy harvested from the sunlight, which eventually turned into fossil fuels in million years, a man-made carbon cycle based on CO<sub>2</sub> was proposed by Olah et al.<sup>2</sup> In the proposed cycle, the CO<sub>2</sub> captured from air or concentrated sources are converted to chemicals and fuels in short time. CO2 is an inexpensive and abundant  $\mathsf{C}_1$  building block. Industrially,  $\mathsf{CO}_2$  is already used to manufacture urea, salicylic acid, cyclic carbonate and polycarbonate.<sup>3</sup> In addition, hydrogenation of CO<sub>2</sub> can produce various chemicals such as, CH<sub>3</sub>OH, CH<sub>4</sub>, HCO<sub>2</sub>H, HCOOCH<sub>3</sub>, depending on the catalyst and the reaction conditions.<sup>4</sup> Among these CO<sub>2</sub> hydrogenated products, CH<sub>3</sub>OH contains high hydrogen weight content (12.5 wt%) and it is also a basic commodity chemical for the synthesis of aromatics, olefins (ethylene and propylene), high-octane gasoline and other chemicals.<sup>5</sup> Current industrial CH<sub>3</sub>OH synthesis is based on a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> heterogeneous catalyst that utilizes a  $CO_2/CO$  and  $H_2$  mixture, which operates at high temperatures (250-300 °C) under high pressures (7 Mpa-10 MPa).6

Since the CH<sub>3</sub>OH formation step is exothermic, low temperature and high pressure favor the selective formation of CH<sub>3</sub>OH (**Scheme 1**). Typically, higher temperatures are required for the hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH using heterogeneous catalysts.<sup>8a</sup> Higher temperature favors the reverse water gas shift (RWGS) reaction and produces CO, which significantly reduces the CH<sub>3</sub>OH yield with respect to CO<sub>2</sub> and it also consumes valuable H<sub>2</sub>. The CO and H<sub>2</sub>O formed from the RWGS reaction is known to have detrimental effect on the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>.<sup>7</sup> Therefore, in order to reduce the production costs and also to utilize the exothermicity of the CO<sub>2</sub>-to-CH<sub>3</sub>OH reaction, it is desirable to perform the reaction at lower temperature.

(a)	CO2 +	$H_2 \rightarrow CH_3C$	$OH + H_2O$	$\triangle$ H° (298K) = -49.4 kJ/mol
(b)	CO <sub>2</sub> +	Н2 СО	+ H₂O	∆Hº (298K) = 41.1 kJ/mol

**Scheme 1.** CH<sub>3</sub>OH formation and RWGS from CO<sub>2</sub> hydrogenation.

The formation of CH<sub>3</sub>OH from CO<sub>2</sub> proceeds via formate (HCOO<sub>ad</sub>), acetal (OCH<sub>2</sub>O<sub>ad</sub>) and methoxy (OCH<sub>3ad</sub>) intermediates.<sup>8</sup> Irrespective of CO<sub>2</sub>/H<sub>2</sub> or CO/CO<sub>2</sub>/H<sub>2</sub> reaction systems, formate is always the reaction intermediate for the CH<sub>3</sub>OH synthesis, and the hydrogenation of formate was identified as a rate-limiting step.<sup>9</sup> In 1995, Noyori et al reported that the addition of alcohol and base promote the homogenous hydrogenation of CO<sub>2</sub> to formate.<sup>10</sup> Similarly, several systems were reported for the homogenous metal catalyzed formate and CH<sub>3</sub>OH synthesis from CO<sub>2</sub> in the presence of alcohols and bases.<sup>11</sup> We note that alcohols and bases promote this reaction as both reagents produce dissolved anionic carboxylates (carbamates and/or alkylcarbonates) from CO<sub>2</sub>,<sup>12</sup> which are electrophilic enough to be reduced by catalysts via an inner sphere mechanism.<sup>12b</sup>

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Formate salts can then undergo thermal condensation to either a formate ester (in the presence of alcohol) or formamide (in the presence of amine), which subsequently get hydrogenated to CH<sub>3</sub>OH (Scheme 2). We note that literature reports cite the need for Lewis acid or base to drive the hydrogenation of formate esters and formamides to CH<sub>3</sub>OH by homogeneous catalysis.<sup>11</sup> We hypothesized that the reactive pathways demonstrated through homogeneous catalysts would be available to heterogeneous catalysts, as the hydrogenations to CH<sub>3</sub>OH have been shown to be catalytic with respect to capture solvent (amine and/or alcohol). Furthermore, the solid-support of heterogeneous catalysts could provide Lewis acid/base sites required for the final hydrogenation of formate esters or formamides to CH<sub>3</sub>OH.<sup>13</sup> The effect of amine and/or alcohol additives on the productivity of the CH<sub>3</sub>OH synthesis catalyst was studied previously using heterogeneous catalysts by different groups. <sup>14</sup> However, most systems reported so far present series of challenges, namely use of CO in the feed gas mixture, require to start from alkylformate ester, stop at alkylformate ester intermediate, undergo decomposition of amines employed, and show low activity/selectivity for CH<sub>3</sub>OH, which is still a major challenge. In order to address these challenges, careful study of reaction pathways is necessary to design a versatile and robust system for CH<sub>3</sub>OH production from CO<sub>2</sub> at low-temperatures with high selectivity/activity.

Herein, we report a lower-temperature condensed phase heterogeneous hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH using only CO<sub>2</sub> as a C<sub>1</sub> source using the commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst at 170 °C under 60 bar CO<sub>2</sub>: H<sub>2</sub>. We utilized both base (amine) and alcohol to promote the formation of CH<sub>3</sub>OH at low-temperature via formamide or formate ester intermediates in the condensed-phase. Thereby we significantly reduced the RWGS reaction and established a new approach for the heterogeneous metal catalyzed CO<sub>2</sub> hydrogenation at low temperature employing inexpensive NEt<sub>3</sub> and EtOH as additives. *Operando* <sup>13</sup>C NMR spectroscopy of this reaction demonstrates the reaction proceed via alkylcarbonate, formate, and formate ester intermediates.

### **Results and Discussion**

 $CO_2$  can be captured from air or concentrated sources by amine, amine/H<sub>2</sub>O, or amine/alcohol mixture to form carbamate, bicarbonate and carbonate respectively (**Scheme 3**).<sup>15</sup> The  $CO_2$ activated by this fashion can either be directly used or it can be released by temperature and/or pressure swing, then compressed and concentrated to produce useful  $CO_2$ -derived products.



Scheme 2. Proposed pathways for the CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH.

In this study, we subjected the *in-situ* formed carbonates and carbamates to hydrogenation. Bicarbonates are not chosen for this study because the presence of  $H_2O$  is known to poison the

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>16,14h</sup> We initially screened 1° and 2° amines, finding that amine bases were hydrogenated to their respective formamides, but were unable to continue to CH<sub>3</sub>OH (entry 1 and 2, **Table S1**). This result indicates that the formamide route (**Scheme 2**, bottom) may not be feasible under these conditions, which we attribute to the low hydride acceptor strength (low electrophilicity) of formamides compared to that of formate esters.



Scheme 3. CO<sub>2</sub> capture using different amines.

Tertiary amines (NEt<sub>3</sub>) were found to be non-reactive, as were alcohol (EtOH), though the combination of 3° amine and alcohol produced CH<sub>3</sub>OH (entry 1-3, **Table 1**). These results suggest that the neutral CO<sub>2</sub> may not be the active species. Thus, we propose that the anionic alkyl carbonate is possibly the active species likely via

Table 1. Hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH

Ent ry	Promoters	Amine: alcohol	HCOO <sup>-</sup>	HCOOEt	CH₃OH
1	NEt₃	-	trace	-	-
2	EtOH	-	-	-	-
3	NEt <sub>3</sub> : EtOH	1:1	trace	trace	2%
4	NEt₃: EtOH	10:1	-	-	-
5	NEt₃: EtOH	1:10	3%	trace	100%
<b>6</b> <sup>a</sup>	NEt₃: EtOH	1:10	3%	1%	76%
7 <sup>b</sup>	NEt₃: EtOH	1:10	-	1%	28%
8 <sup>c</sup>	NEt <sub>3</sub> : EtOH	1:10	4%	4%	19%
9	NEt₃: EtOH	1:5	trace	trace	7%
10	TMEA:EtOH	1:10	-	1%	18%
11	DEEA:EtOH	1:10	0.5%	trace	21%

Standard reaction conditions: Catalyst=Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (300 mg), CO<sub>2</sub>/H<sub>2</sub>=60 bar (1:2), EtOH (200 mmol), amine (20 mmol), T=170 °C t=16h. HCOO<sup>-</sup>, HCOOEt and CH<sub>3</sub>OH yield are based on <sup>1</sup>H NMR. The yields are calculated with respect to the amine. <sup>a</sup>40h, <sup>b</sup>150°C and <sup>c</sup>120°C

the observed coordination to the cationic metal surface by which hydrogenation to  $HCO_2H$  occurs, *vide infra*. The methanol conversion is reported against the amount of amine as it provides a readily available internal standard to calculate against. NEt<sub>3</sub> and EtOH produced CH<sub>3</sub>OH at 2% conversion with respect to NEt<sub>3</sub> (entry 3, **Table 1**). While the tertiary alkanolamines, N,N,N',N'-tetrakis(2hydroxyethyl) ethylenediamine (THEED) and triethanolamine (TEA) decomposed at high temperature (entry 4 and 5, **Table S1**). Diethylethanolamine (DEEA) however, produced 6.5 mmol of CH<sub>3</sub>OH (4% conversion based on amine, entry 6, **Table S1**). Unexpectedly, Proton-sponge and Bisphenol A underwent partial hydrogenation of aromatic ring (entry 7 and 8, **Table S1**) and were not tested further.

Changing the ratio of amine to alcohol influenced the conversion to CH<sub>3</sub>OH; if the ratio of amine to alcohol was 10:1, the conversion of CH<sub>3</sub>OH with respect to amine is poor, whereas a ratio of 1:10 enables a 100% conversion to CH<sub>3</sub>OH with respect to amine (entry 4 and 5, Table 1). The CH<sub>3</sub>OH synthesis activity as high as 4166 mmol/(Kg-cat-h) was obtained at 170 °C with a CH<sub>3</sub>OH yield of ~10% with respect to CO<sub>2</sub>. An excess of NEt<sub>3</sub> could passivate the catalyst surface and limiting the reaction. It is likely that polarity has a strong influence on the reactivity as we have shown the formation of alkylcarbonates to be highly sensitive with respect to polarity.<sup>15a</sup> The relatively lower polarity of NEt<sub>3</sub> would disfavor the formation of the highly polar alkylcarbonate, whereas an excess of alcohol would be polar enough to favor alkylcarbonate formation. Further EtOH could solvate polar transition states and charged intermediates common to CO<sub>2</sub> hydrogenations whereas NEt<sub>3</sub> would not. Excess alcohol would also promote the thermal esterification to produce formate ester. Gas chromatographic analysis of the gas mixtures only showed trace of  $CH_4$  and CO in addition to excess  $H_2$  and  $CO_2$ .

### Table 2. Effect of basicity of amine on the carbonate formation

Entry	Amine	рКа	Methyl	IR (CO)	<sup>13</sup> C NN	<sup>13</sup> C NMR (ppm)	
			carbonate (%)	cm <sup>-1</sup>	la	II <sup>b</sup>	
1	DBU	12	98	1642	52.2	159.8	
2	DIPEA	11.4	92	1647	51.1	158.8	
3	NEt <sub>3</sub>	10.6	75	1654	52.3	160.1	
4	DMAP	9.9	64	1651	52.4	160.5	
5	DABCO	8.8	64	1650	49.1	160.0	
6	Pyridine	5.5		No	o reactio	n	

Standard reaction conditions: (A) alkylcarbonate formation from  $CO_2$  capture –alkylcarbonate yield calculated with respect to amine by <sup>13</sup>C NMR of 2M amine in CH<sub>3</sub>OH under 10 bar  $CO_2$  at RT, <sup>a</sup>NMR resonance of methyl carbon in CH<sub>3</sub>OCOO<sup>-</sup> species, <sup>b</sup>NMR resonance of carbonate carbon in CH<sub>3</sub>OCOO<sup>-</sup> species. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, DIPEA = N,N-Diisopropylethylamine, DMAP = 4-Dimethylaminopyridine, DABCO = 1,4-diazabicyclo[2.2.2]octane

The necessity for the combination of non-nucleophilic bases and alcohols suggests CH<sub>3</sub>OH production proceeds via the formate and formate ester route (Scheme 2). The presence of amine and alcohol promotes the formation of alkylcarbonate, ammonium formate and alkyl formate ester intermediates. Under optimal conditions, the amount of CH<sub>3</sub>OH produced never surpassed the amount of amine used regardless of time, which is suggestive of an established equilibrium (entry 6, Table 1). Even at lower temperatures 150 °C and 120 °C, moderate CH<sub>3</sub>OH yields were obtained (entry 7 and 8, Table 1) suggesting that the reaction does not necessarily need to proceed at 170 °C. Tetramethylethylenediamine (TMEA) and DEEA formed 18% and 21% CH<sub>3</sub>OH respectively in presence of excess EtOH (entry 10 and 11, table 1). From entry 11, Table 1 and entry 6, Table S1, it is clear that the presence of excess alcohol does not improve the amount of CH<sub>3</sub>OH formed in the case of DEEA base as it decomposes under these conditions.

We then studied the effect of basicity on alkylcarbonate formation capacity of the amines and alcohols on the  $CH_3OH$ formation. The alkylcarbonate formation in **Table 2** was studied under high pressure since some alkylcarbonates are not stable under atmospheric conditions. From **Table 2**, it is clear that the strong bases give high methyl carbonate yield, however with low CH<sub>3</sub>OH yield (**Figure 1**). While less basic amines give moderate methyl carbonate yield but high CH<sub>3</sub>OH yield. NEt<sub>3</sub> showed the highest CH<sub>3</sub>OH yield, suggesting a pKa of the conjugate acid above or below 11 (in H<sub>2</sub>O) is optimal under these conditions. Since aromatic ring hydrogenation was observed in the presence of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst (*vide supra*), DMAP and pyridine were not chosen for the CO<sub>2</sub> hydrogenation study.

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ARTICLE

### Table 3. Effect of alkyl chain length and sterics of alcohol on the

Entry	Alcohol (%)	рКа	Alkyl carbonate (%)
1	CH₃OH	16	75
2	EtOH	15.9	75
3	<i>i</i> -propanol	16.5	25
4	Ethyleneglycol <sup>a</sup>	14.2	35
5	<i>t</i> -Butanol	17	No reaction
6	Phenol <sup>b</sup>	10	No reaction

### carbonate formation

Standard reaction conditions: Alkylcarbonate formation from CO<sub>2</sub> capture –alkylcarbonate yield calculated with respect to amine by  $^{13}C$  NMR of 2M NEt<sub>3</sub> in alcohol under 10 bar CO<sub>2</sub> at RT,  $^a$ Only one OH group is carbonated.  $^b$ the reaction was performed in THF.



Figure 1. Standard reaction conditions: (A) Alcohols: catalyst=Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (300 mg), CO<sub>2</sub>/H<sub>2</sub>=50 bar (1:2), EtOH (200 mmol), amine (20 mmol), T=170 °C, t=16h, (B) Amines: catalyst=Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (300 mg), CO<sub>2</sub>/H<sub>2</sub>=50 bar (1:2), alcohol (200 mmol), NEt<sub>3</sub> (20 mmol), T=170 °C, t=16h, CH<sub>3</sub>OH yield calculated with respect to amine.

Similarly, the choice of alcohol on the alkylcarbonate was investigated under pressure (**Table 3**). The presence of  $CH_3OH$  or EtOH did not show significant difference in the alkylcarbonate yield, which is contributed to similar pKa's of the alcohols. However, the alkyl chain length and sterics significantly reduced the alkylcarbonate conversion and  $CH_3OH$  yields (**Figure 1**). This result is consistent with our previous observations that secondary alcohols do not form as much alkylcarbonate as linear alcohols because of steric crowding.<sup>17</sup> Similarly, phenol is likely not electrophilic enough to attack  $CO_2$  and doesn't carboxylate under these conditions (entry

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Journal Name

### ARTICLE

6, **Table 3**). The results obtained from **Table 2**, **Table 3** and **Figure 1** suggests that the 3° amines and short linear alcohols are the best combination for high  $CH_3OH$  yield, consistent with conditions that favor alkylcarbonate formation.



 $\mbox{Scheme 4}.$  Plausible reaction mechanism for the one-pot  $\mbox{CO}_2$  capture and conversion.

While a direct correlation between the alkylcarbonate formed and CH<sub>3</sub>OH formation was observed (Table 2 and Table 3), it is expected that there is a small amount of alkylcarbonate present at 170 °C under 25 bar CO2. Based on our observations and the literature studies<sup>18</sup>, we propose a plausible reaction mechanism via coordination of anionic ethyl carbonate to the catalyst surface, by which the reaction proceeds via formate and ethylformate intermediates (Scheme 4). Catalyst recycling was studied under 1:2  $CO_2:H_2$  pressure. In the second run, some drop in catalytic activity was observed. However, the activity remained the same in the third run. The decrease in the catalytic activity was probably due to the catalyst sintering, which was confirmed by powder X-ray diffraction (XRD) - performed after the third run (Scheme S7). The Cu particle size increased from 21 nm (freshly reduced) to 40 nm (spent). Similar sintering of catalyst in the batch reactor was observed previously in the presence of  $H_2O$ , the byproduct.<sup>7</sup> XRD analysis also showed the presence of ZnCO<sub>3</sub>, which could have formed from an excess CO2 concentration under pressurized conditions.<sup>19</sup> Thus, changes in activity could be explained by both sintering of the Cu particles and due to phase change of the ZnO support. However, at this point of the study, it is not clear whether ZnCO3 is involved in the active catalytic cycle. We note that inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the solution after the hydrogenation showed minimal catalyst leaching (Cu=2.2 ppm, Zn=5.1 ppm, Al=<1.3 ppm)."





Figure 2. In-situ  $^{13}C$  MAS NMR of the reaction mixture (NEt\_3:10EtOH,  $^{13}CO_2$  and H<sub>2</sub>) in the presence of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> at 170 °C, 1h.

High temperature operando <sup>13</sup>C magic angle spinning (MAS) NMR study of the catalyst in the presence of 1:10 NEt<sub>3</sub> and EtOH mixture at 20 bar of CO<sub>2</sub> at 120 °C showed ethylcarbonate (158.9 ppm) at a concentration 2.2 times that of the active sites on the catalyst. We also observed ethylcarbonate bound to the catalyst (165.7 ppm) at a concentration that is 22% of the active site calculated for the catalyst (**Figure S2**). 19% conversion to CH<sub>3</sub>OH was observed at 120 °C (**Table 1**) indicating ethylcarbonate exists in a significant enough concentration to participate in the reaction at least up to this temperature.

*Operando* <sup>13</sup>C MAS NMR at 170 °C in the presence of  $H_2$  did not show a detectable amount of ethylcarbonate, though it clearly showed the formation of triethylammonium formate (168.5 ppm) as an initial intermediate, which then converted to ethyl formate (161.2 ppm). CH<sub>3</sub>OH signal at 48.7 ppm started to grow quickly in less than 5 min of heating at 170 °C (**Figure 2**). Over time CH<sub>3</sub>OH decomposed into CO (182.2 ppm), confirming the hydrogenation does not proceed via CO.

H <sup>13</sup> COOEt	~CO2	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N	CH <sub>2</sub> OH CH <sub>3</sub> CH <sub>2</sub> OH (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N	
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**Figure 3.** *In-situ* <sup>13</sup>C MAS NMR of the reaction mixture (NEt<sub>3</sub>:10EtOH,  $^{13}CO_2$  and H<sub>2</sub>) in the presence of Pd/ZnO at 170 °C, 15h.

We also studied the  $CO_2$  hydrogenation via the ammonium formate and alkyl ester intermediates in the presence of Pd/ZnO catalyst under the same conditions studied previously for the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. Though Pd/ZnO was well-studied in the

### Journal Name

literature for CH<sub>3</sub>OH formation via CO route (>250 °C),<sup>20</sup> there was no detectable amount of CH<sub>3</sub>OH observed by <sup>13</sup>C NMR at 170 °C. However, slow accumulation of alkyl formate was observed overtime (**Figure 3**).

### Conclusions

We have demonstrated a low-temperature condensed phase heterogeneous hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH using NEt<sub>3</sub> and EtOH. The formation of side products such as CO and CH<sub>4</sub> are significantly reduced. Screening of various amines and alcohols revealed that the alkyl carbonate, ammonium formate and alkyl ester are the key intermediates involved in the reaction which was confirmed by *Operando* <sup>13</sup>C MAS NMR. The degree of alkyl carbonate and methanol formation were found to be limited by polarity of solvents as well as basicity of the amine. Performing the present reaction in a flow system could significantly improve the overall productivity of the system, as poisoning of catalyst arising from the accumulation of products would be minimal.

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