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ARTICLE

Synthesis of Ethanol via Reaction of Dimethyl Ether with CO_2 and H_2

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Ethanol is currently produced via catalytic hydration of ethylene or fermentation of foods. Synthesis of ethanol from cheap and renewable CO_2 is of great importance, but state of the art routes encounter difficulties, especially in reaction selectivity and activity. Here we show a strategy of ethanol synthesis from CO_2, dimethyl ether (DME) and H_2. The reaction can be effectively promoted by Ru-Co bimetallic catalyst using LiI as promoter in 1,3-dimethyl-2-imidazolidinone (DMI) solvent. The predominant product of this reaction was ethanol and the selectivity of ethanol in total products could reach 71.7 C-mol%. The selectivity of ethanol in liquid product could reach 94.1%, which was higher than the reported routes using CO_2/CO. To the best of our knowledge, this is the first work on ethanol synthesis from DME, CO_2 and H_2. The reaction mechanism was discussed based on a series of control experiments.

Introduction

Ethanol as an alternative fuel has been widely utilized in current energy infrastructure.[1] It is also a very important bulk chemical. Currently, ethanol is mainly produced via catalytic hydration of ethylene from fossil raw materials or fermentation of foods such as corn and sugar.[2] CO_2 is a greenhouse gas and its fixation into value-added products is highly desirable for sustainable development of our society.[3] To date, CO_2 has been used as a building block to synthesize various chemicals, such as urea, polymers, carboxylic acids, carbonates, amides and alcohols.[4,5] As for the synthesis of alcohols using CO_2 as a feedstock, the major research progress has been focused on methanol in the past decades.[6] Efficient synthesis of ethanol, is certainly of great importance, but is more difficult due to selective C-C coupling.

The previous reports of ethanol production from CO_2 were mostly confined to direct CO_2 hydrogenation at high temperatures (>250 ^{o}C).[7-13] In such reports, CO_2 usually reacted with H_2 to generate reactive C_1 intermediates, say CO, CH_3 and/or CH_3OH, then the C-C bond formation steps took place to generate C_{2+} products, such as ethanol and higher alcohols.[10,11,14-17] Because the in situ formation of C_1 intermediates and the C-C bond construction occurred simultaneously, the reaction products usually consisted of various alcohols and hydrocarbons. In addition, the ethanol selectivity in the total products was generally low (< 20 C-mol%). To raise the ethanol selectivity, introducing certain substrate to react with CO_2 and H_2 is a feasible way. When methanol reacted with CO_2 and H_2, ethanol was the only alcohol product and 34.2 C-mol% of ethanol selectivity in total products (CO 46.5 C-mol%, methane 19.3 C-mol%) was obtained.[18a] In addition, the space time yield (STY) of the reaction reached 124.9 C-mmol $L^{-1}h^{-1}$. Paraformaldehyde could also reacted with CO_2 and H_2 to produce ethanol, during which paraformaldehyde was firstly converted into methanol.[18b] Currently, CO_2 hydrogenation with simultaneous C-C bond formation is still a grand challenge in CO_2 chemistry.[19] Recently, elegantly designed and highly ordered Pd-Cu nanocatalyst was prepared, and it was discovered that the selectivity of ethanol could reach 92.0%.[20] Although significant progress has been achieved in this interesting area, exploration of new strategy to produce ethanol efficiently from CO_2 under milder condition using easily prepared catalysts is still highly desirable.

Dimethyl ether (DME) is a cheap and bulk chemical, which can be produced in a single-stage process from CO_2/CO and H_2. DME is also a key intermediate to bulk chemicals in industry (e.g., acetic acid, olefins, hydrocarbons).[2] Here we show a protocol to produce ethanol from DME, CO_2 and H_2 (Scheme 1). The reaction can proceed efficiently over $Ru(PPh_3)_3Cl_2/CoI_2$ bimetallic homogeneous catalyst at mild condition. Very interestingly, this reaction has very high ethanol selectivity. It is confirmed that the ethanol synthesis is through direct participation of DME (not via methanol or methyl iodide) and/or synergy of catalyst components, accounting for the distinguished catalytic results. This strategy represents an important progress in CO_2 chemistry and opens a promising way to fix CO_2 into fuels and bulk chemicals.

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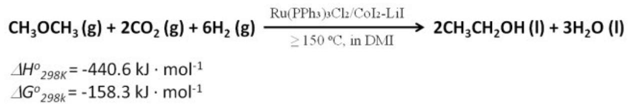

Scheme 1. Synthesis of ethanol via reaction of DME with CO_2 and H_2. The thermodynamic data were from Lange's Handbook of Chemistry (13th Edition, J. A. Dean Ed., McGraw-Hill Book Company, 1985)

Results and discussion

Catalytic system for ethanol synthesis. The reaction could be efficiently catalyzed by $Ru(PPh_3)_3Cl_2$ and CoI_2 bimetallic catalyst using LiI as promoter in 1,3-Dimethyl-2-imidazolidinone (DMI) at milder conditions. In this work, ethanol was the product, and methanol, CO, and methane were the only by-products. The selectivity of the product and all the by-products are given in Table 1. Ethanol was the predominant product in the reaction solution with little methanol as byproduct (Figure S1a). Very interestingly, only minor CO and methane was detected in the gaseous sample (Figure S1b). The STY of the reaction was as high as 132.5 C-mmol $L^{-1}h^{-1}$ and the selectivity of ethanol was 71.7 C-mol% (Entry 1). The selectivity of ethanol in liquid product could reach 94.1%, which was higher than the reported routes using CO_2/CO. Some representative reports of ethanol synthesis from CO_2 are listed in Table S1.

The promoter was indispensable in this reaction. No alcohol was generated and the catalytic system was not stable without promoter (Entry 2). When the promoters with other cations (K^+, Zn^{2+}) or anions (Cl^-, BF_4^-) were used, the results were poor (Entries 3-6). Hence LiI was the best promoter in accelerating the target reaction. The strong Lewis acidity and small size of Li^+ may be beneficial to coordinating and/or activating DME molecule.[21] It is well known that iodide anion is an eminent ligand for transition metal catalysts, which may effectively tailor the stability, selectivity and activity.[22] The I^- helped to maintain the catalyst stability (Entries 1, 6). In addition, the larger size of iodide compared to other halides has more remarkable steric effect, resulting in better catalytic selectivity (Entries 1, 5).

We tried $Ru(PPh_3)_3Cl_2$ or CoI_2 as the single catalyst respectively, but the results were poor (Entries 7,8). Obviously, synergic effect existed between Ru and Co catalysts during the catalytic reaction. The precursors of the Ru-Co bimetallic catalyst were crucial for the catalytic performance. When we

Table 1. Synthesis of Ethanol via reaction of DME with CO_2 and H_2 using different catalytic systems.[a]

Entry	Catalyst precursor	Promoter	Solvent	STY[c]	Selectivity [C-mol%]			
					Ethanol	Methanol	CO	CH_4
1[d]	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	DMI	132.5	71.7	4.5	13.8	10.0
2[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	-	DMI	7.1	0.0	0.0	70.6	29.4
3	$Ru(PPh_3)_3Cl_2$, CoI_2	KI	DMI	80.4	39.9	7.3	40.4	12.4
4[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	ZnI_2	DMI	15.0	36.1	19.4	41.7	2.8
5	$Ru(PPh_3)_3Cl_2$, CoI_2	LiCl	DMI	56.3	8.9	10.6	71.7	8.8
6[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	$LiBF_4$	DMI	38.3	14.1	20.6	37.0	28.3
7	$Ru(PPh_3)_3Cl_2$	LiI	DMI	42.5	0.4	5.5	83.3	10.8
8	CoI_2	LiI	DMI	9.2	2.5	20.2	40.9	36.4
9[b]	$Ru(acac)_3$, CoI_2	LiI	DMI	80.4	36.1	6.7	23.8	33.4
10	$Ru_3(CO)_{12}$, CoI_2	LiI	DMI	93.8	41.6	4.0	25.3	29.1
11	$Ru(PPh_3)_3Cl_2$, $CoCl_2$	LiI	DMI	34.6	0.0	13.3	56.6	30.1
12	$Ru(PPh_3)_3Cl_2$, $Co_4(CO)_{12}$	LiI	DMI	20.8	0.0	28.0	60.0	12.0
13	$Ru(PPh_3)_3Cl_2$, $Rh_2(CO)_4Cl_2$	LiI	DMI	27.5	27.3	19.7	42.4	10.6
14	$Ru(PPh_3)_3Cl_2$, $Ir_4(CO)_{12}$	LiI	DMI	47.5	6.2	9.6	75.4	8.8
15	$Ru(PPh_3)_3Cl_2$, Ferrocene	LiI	DMI	44.2	11.3	11.3	65.1	12.3
16[b]	$NiCl_2$, CoI_2	LiI	DMI	45.4	23.0	22.0	12.8	42.2
17[b]	$Mn_2(CO)_{10}$, CoI_2	LiI	DMI	15.0	5.6	63.9	19.4	11.1
18[b]	$CuSO_4$, CoI_2	LiI	DMI	12.9	0.0	45.1	19.4	35.5
19[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	$N(C_3H_7)_3$	15.4	0.0	0.0	97.3	2.7
20	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	N-methylpyrrolidine	9.6	0.0	0.0	91.3	8.7
21[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	cyclohexanone	87.9	0.0	13.3	0.0	86.7
22	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	2-Pyrrolidinone	19.2	0.0	0.0	93.5	6.5
23	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	NMP	84.2	39.1	5.4	32.7	22.8
24[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	Cyclohexane	44.6	0.0	0.0	0.0	100.0
25[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	Benzene	45.4	0.0	15.6	0.0	84.4
26[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	DMF	42.9	0.0	0.0	96.1	3.9
27[b]	$Ru(PPh_3)_3Cl_2$, CoI_2	LiI	Water	29.6	0.0	76.1	14.0	9.9

[a] Reaction condition: 30 μmol Ru catalyst and 70 μmol Co catalyst (based on the metal), 2.3 mmol promoter, 2 mL solvent, 0.5 MPa DME (4 mmol), 4 MPa CO_2 (30 mmol) and 4 MPa H_2 (32 mmol) (at room temperature), 180 °C and 12 h. [b] Precipitate was observed after the reaction. [c] STY stands for space time yield (C-mmol $L^{-1}h^{-1}$), which is one of the commonly used units, especially when multi-metals are utilized. [d] The conversion of DME in Entry 1 was 20.6%, and the conversions of DME at other conditions were lower than that of entry 1.

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utilized Ru(acac)$_3$ or Ru$_3$(CO)$_{12}$ instead of Ru(PPh$_3$)$_3$Cl$_2$ to conduct the reaction, the catalytic activity was much lower (Entries 9,10). We also used CoCl$_2$ or Co$_4$(CO)$_{12}$ instead of CoI$_2$, but the catalytic activity was very low and no ethanol was generated (Entries 11,12). When we combined Ru(PPh$_3$)$_3$Cl$_2$ with other metal (Rh, Ir, Fe) complexes, the results were not satisfactory (Entries 13-15). We also combined CoI$_2$ with other metal (Ni, Mn, Cu) compounds, the catalytic performance was also not satisfactory (Entries 16-18). Thus, the Ru(PPh$_3$)$_3$Cl$_2$ and CoI$_2$ cooperated very well for the target reaction.

The solvent also played an important role in the target reaction. It is known that DMI is a cyclic diamine with a ketone group. Using Ru(PPh$_3$)$_3$Cl$_2$/CoI$_2$ as catalyst and LiI as promoter, we studied the solvent effect of the reaction. To study the role of the amine group on solvent molecule, we firstly used tripropylamine as solvent, but no ethanol was detected and the catalyst decomposed significantly (Entry 19). Then we tried a cyclic amine, N-methylpyrrolidine, no ethanol was generated either, but the catalyst was stable (Entry 20). So the cyclic amine is beneficial to the stability of the catalyst. To investigate the effect of the ketone group, we utilized the cyclohexanone as solvent, whereas no ethanol was detected and the catalyst was unstable (Entry 21). When 2-Pyrrolidinone, which combines cyclic amine and ketone group, was applied as solvent, the catalyst was stable, but no ethanol was formed either (Entry 22). Ethanol was produced and the catalyst was stable when N-methyl-2-pyrrolidone (NMP) was used as the solvent (Entry 23). Thus, it can be deducted that the cyclic amine with N-methyl group and ketone group in the solvent benefits the reaction. DMI has not only similar molecular structure with NMP, but also has one more amine group with the N-methyl, and it was a better solvent for the reaction than NMP (Entries 1 and 23), suggesting that both of the amine groups with N-methyl in DMI could effectively improve the reaction activity and selectivity. We also tested other solvents, such as cyclohexane, benzene, DMF and water, but the results were poor (Entries 24-27). In brief, the catalytic system composed of Ru(PPh$_3$)$_3$Cl$_2$/CoI$_2$, LiI and DMI showed better performance than other catalytic systems tested in the work.

Effect of reaction parameters. Based on the optimized catalytic system, we investigated the impact of reaction temperature, pressure, and dosage of each catalyst component on the catalytic reaction. The yields of the products at different temperatures were depicted in Figure 1. No product was detectable when the reaction was conducted at 140 °C, and obvious ethanol emerged when the temperature was increased to 150 °C. The reaction rate increased rapidly with the increasing temperature until 180 °C. The STY of the reaction at 180 °C was 132.5 C-mmol L^{-1}h^{-1} and its growth became slower when the temperature was further raised. The selectivity of ethanol increased steadily with the elevation of temperature until 180 °C. The ethanol selectivity was 71.7 C-mol% at 180 °C, while it decreased evidently with further elevating temperature. This may be attributed to evident yield of methane at higher temperatures.

The data in Figure 1 demonstrate that 180 °C was an appropriate temperature. We further investigated the impact of other parameters on the reaction at this temperature, and the results are given in Table 2. The pressure of CO$_2$ and H$_2$ influenced the reaction significantly. At the fixed ratio of CO$_2$ and H$_2$ (1/1), both the reaction rate and the ethanol selectivity grew remarkably when the total pressure was enhanced from 2 MPa to 8 MPa (Entries 1-4). They were not sensitive to the total pressure at higher pressure (Entry 5). At a fixed total pressure of 8 MPa, the ratio of CO$_2$ and H$_2$ also affected the reaction and the best result was obtained at the ratio of 1/1 (Entries 4,6,7). When we tried the experiments without CO$_2$ and/or H$_2$, no alcohol was produced (Entries 8,9,10). Thus CO$_2$ and H$_2$ are both indispensable for the reaction. The dosage of LiI also evidently impacted the reaction activity and selectivity (Entries 4,11,12), and the best performance was obtained when the dosage of LiI was 2.3 mmol. The result revealed that excess amount of LiI was not favorable to the reaction, which may be due to the occupation of the active sites by the excess iodide anions.

The atom ratio of Ru and Co also affected the reaction remarkably. At the same total amount of metals (100 μmol), 30 μmol Ru and 70 μmol Co yielded the best catalytic result (Entries 4,13,14). The total catalyst dosage also influenced the

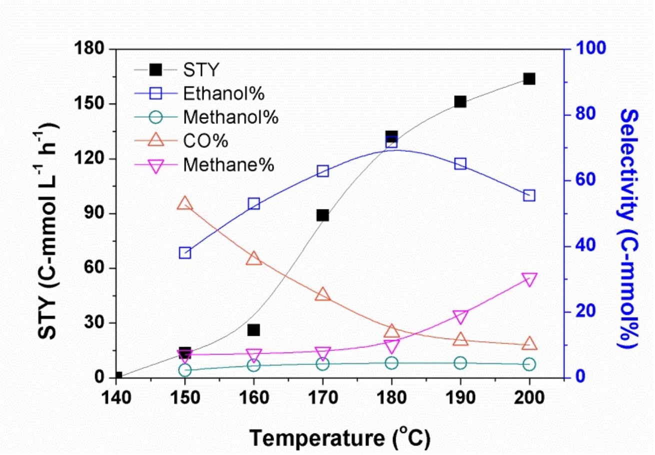

Figure 1. The yield of products at different temperatures. Reaction condition: 30 μmol Ru(PPh$_3$)$_3$Cl$_2$ and 70 μmol CoI$_2$, 2.3 mmol LiI, 2 mL DMI, 0.5 MPa DME, 4 MPa CO$_2$ and 4 MPa H$_2$ (at room temperature), 12 h.

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Table 2. Effect of reaction parameters on ethanol synthesis from DME with CO_2 and H_2.[a]

Entry	Ru/Co [μmol]	LiI [mmol]	CO_2/H_2 [MPa]	STY	Selectivity [C-mol%]			
					Ethanol	Methanol	CO	CH_4
1	30/70	2.3	1/1	15.8	31.6	36.8	23.7	7.9
2	30/70	2.3	2/2	32.9	46.8	15.2	29.1	8.9
3	30/70	2.3	3/3	83.8	67.2	6.5	18.3	8.0
4	30/70	2.3	4/4	132.5	71.7	4.5	13.8	10.0
5	30/70	2.3	5/5	144.6	73.3	4.4	12.6	9.7
6	30/70	2.3	2/6	103.3	68.2	1.5	19.8	10.5
7	30/70	2.3	6/2	23.8	35.1	5.3	49.1	10.5
8	30/70	2.3	0/4	29.2	0.0	0.0	0.0	100.0
9	30/70	2.3	4/0	0.0	-	-	-	-
10	30/70	2.3	0/0	0.0	-	-	-	-
11	30/70	1.15	4/4	85.0	63.2	7.8	22.1	6.9
12	30/70	3.45	4/4	66.7	40.6	5.6	40.0	13.8
13	15/85	2.3	4/4	110.0	65.9	6.1	24.2	3.8
14	45/55	2.3	4/4	121.3	68.5	7.9	15.4	8.2
15	15/35	2.3	4/4	92.5	71.6	7.2	16.7	4.5
16	45/105	2.3	4/4	85.0	63.7	6.8	22.1	7.4
17[b]	30/70	2.3	4/4	21.3	0.0	0.0	98.7	1.3
18[c]	30/70	2.3	4/4	34.2	54.9	6.1	31.7	7.3
19	0/0	2.3	4/4	14.6	0.0	28.6	48.5	22.9
20	30/0	0	4/4	22.5	0.0	0.0	100.0	0.0
21	0/70	0	4/4	5.4	0.0	69.2	0.0	30.8
22[b,d,]	30/70	2.3	4/4	0.5	0.0	0.0	0.0	100.0

[a]Reaction conditions: $Ru(PPh_3)_3Cl_2/CoI_2$ were used as the catalysts and their dosage was based on the metal, LiI was used as the promoter, 2 mL DMI, DME 0.5 MPa (at room temperature), 180 °C, and 12 h. [b]No DME was added in the reaction. [c]Water (2 mmol) was added before reaction. [d]CO was used instead of CO_2.

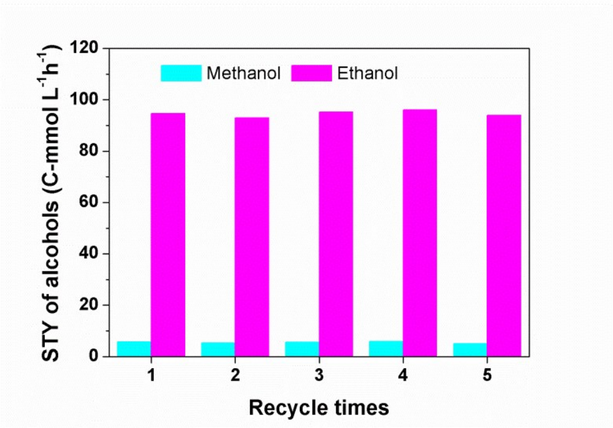

Figure 2. The results of the recycling test. Reaction condition: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 0.5 MPa DME, 4 MPa CO_2 and 4 MPa H_2 (at room temperature), 180 °C and 12 h.

reaction. When we fixed the ratio of Ru and Co at 3/7 and changed the total amount of the catalysts, the best dosage of the catalysts was also 30 μmol Ru and 70 μmol Co (Entries 4, 15, 16). Therefore, the dosage of the catalysts (30 μmol Ru and 70 μmol Co) was fixed for further investigation.

Recyclability. To investigate the reusability of the catalytic system, the alcohols generated in the reactor was removed at 80 °C for 3 h in a vacuum oven, then GC analysis confirmed that the alcohols in catalytic system were negligible, and the catalytic system was used directly for the next run. Figure 2 reveals that the yield of alcohols did not change obviously after five cycles.

Time course of the reaction. Figure 3 illustrates the time course of the reaction. The amount of ethanol increased slowly at the beginning (0-3 h), then grew rapidly until 12 h, and the increase of the ethanol production became slower after 12 h. In the whole course, the amount of methane grew slowly and its amount was small compared to that of ethanol. In addition, the content of CO and methanol, which are usually known as intermediates of the ethanol synthesis from CO_2, were nearly kept constant after the initial period. While in the reported routes, CO and/or methanol tend to increase at the beginning of the reaction and decrease with the time going on.[14-16] This indicates that the reaction would follow a different reaction pathway.

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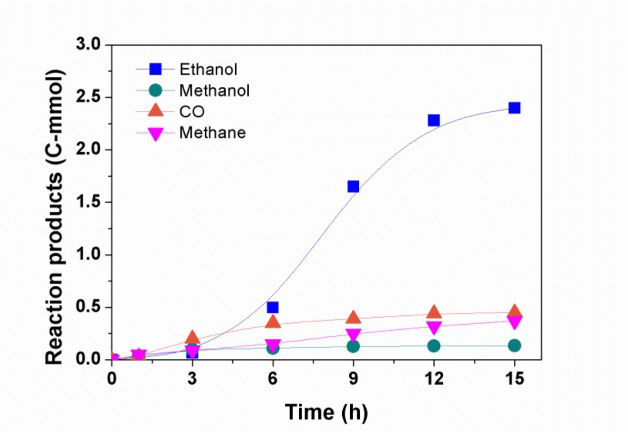


Figure 3. The time course of the reaction of DME with CO_2 and H_2. Reaction condition: 30 μmol $Ru(PPh_3)_3Cl_2$ and 70 μmol CoI_2, 2.3 mmol LiI, 2 mL DMI, 0.5 MPa DME, 4 MPa CO_2 and 4 MPa H_2 (at room temperature), 180 °C.

Reaction Pathway. In this work DME is necessary for the formation of alcohols. Without DME, no alcohol was formed (Entry 17 of Table 2 and Figure S2a). In the reported routes, methanol is a common intermediate for the synthesis of ethanol.[14-16] It is well known that DME may transform into methanol via hydration over acids.[23] If methanol was the intermediate of the target reaction, water in the reactor would promote the reaction. To clarify this possibility, we added water before the reaction but the reaction was significantly inhibited (Entry 18 of Table 2). Moreover, in the presence of H_2, DME could not effectively transform into methanol, while methanol converted into DME evidently (Entry 8 of Table 2 and Figure S3, Figure S4). These may be because the DMI solvent rendered a basic condition and suppressed the conversion of DME into methanol. We also found that methanol generated by individual component (Ru catalyst, Co catalyst or LiI) or their combinations (Ru/Co, Ru/LiI or Co/LiI) was little or undetectable (Entries 2,7,8 of Table 1 and Entries 19-21 of Table 2), suggesting that DME (not via methanol) directly participated in the formation of ethanol. When we used methanol to react with CO_2 and H_2, considerable methane was produced and the selectivity of ethanol was much lower (Figure S5). All the results ruled out the possibility that methanol was the major intermediate for formation of ethanol in the reaction.

Usually, CH_3I is a key species for the C-C bond formation from methanol.[5a,14,18] CH_3I could form spontaneously in the presence of methanol and iodide/iodine at elevated temperatures.[24] To make clear whether the DME transformed into CH_3I during the reaction, we conducted the reaction of DME and LiI at the reaction temperature, but no CH_3I was observed (Figure S6). We further used CH_3I as substrate to react with CO_2 and H_2, but it mostly turned into methane and no ethanol was observed (Figure S7). It can be deduced that CH_3I is not reactive intermediate of the target reaction of this work, which is in accordance with the previous report of DME homologation with syngas (CO/H_2).[25] The lack of methanol and/or CH_3I intermediates in the reaction could effectively reduce the generation of methane.

As a byproduct, CO was detected after CO_2 hydrogenation catalyzed by our reaction system (Figure S2b). CO is also regarded as an usual intermediate in ethanol synthesis from CO_2, which is generated via reverse water gas shift reaction (RWGS).[14-18] To make clear of this possibility, we firstly used CO and H_2 to conduct the reaction, but no alcohol was generated (Entry 22 of Table 2 and Figure S8a). While remarkable ethanol was produced when DME reacted with CO and H_2, in the presence of water (Figure S9). To study whether other C_1 species formed by CO_2 and H_2 participated in the ethanol synthesis, we used formaldehyde and formic acid to react with DME, respectively. The results revealed that no ethanol was detected, but significant methane, H_2 and CO_2 were observed due to decomposition of formaldehyde or formic acid (Figures S10 and S11). These facts affirmed that CO was the intermediate to react with DME and H_2 in the target reaction. In the reported ethanol synthesis from DME and syngas (CO/H_2), methanol was usually the major product although dual bed composite catalysts were utilized at high temperature (≥220 °C).[26] In addition, evident methyl acetate and ethyl acetate were observed. While in this work ethanol was the predominant product and no acetate was detected (Figure S1a).

Isotopic tracer experiments. To further understand the target reaction, we conducted the tracer test using $^{13}CO_2$ and D_2, respectively. The tracer test using $^{13}CO_2$ showed that the C atom in the methyl group (CH_3-) of ethanol was from DME, while the other C atom (-CH_2OH) was from CO_2 (Figure S12). The NMR spectra of the reaction solution using $^{13}CO_2$ also supported the above conclusion (Figure S13). In addition, the C atoms in the methanol and CO originated from DME and CO_2 respectively (Figure S12). In CO_2 hydrogenation or CO hydrogenation, methane was hardly detectable (Entries 17 and 22 of Table 2, Figure S2b and Figure S8b). So the major origin of methane should be from DME (Entry 8 of Table 2, Figure S3b).

The results using D_2 as tracer showed that D_2 entered into the molecules of methanol and ethanol during the reaction (Figures S14 and S15). Obviously, evident H-D exchange between D_2 and the H atoms in original DME molecules took place. The number of D atoms in the product increased with the elevated D_2 pressure. The mass spectra affirmed that the methanol and ethanol molecules produced in the reaction could totally consist of C and D elements, especially at higher D_2 pressure. The H atoms in the unreacted DME molecules were intact. It can be deduced that the hydrogen isotope (H-D) exchange reactions proceeded during the activation and/or conversion steps. The detailed study of such exchange reactions has been reported elsewhere.[27] Based on the above discussion, we proposed the origin of C and H atoms in the reaction products (Figure 4).

Mechanism. Based on all the results above, we proposed the possible mechanism of the reaction, as is shown in Scheme 2. Firstly, DME coordinated with Li^+ (Step **1**), during which the CH_3-O bond became weaker.[21] The activated DME could form CH_3Co^* with the active Co species (Co^*), as shown in Step **2**.

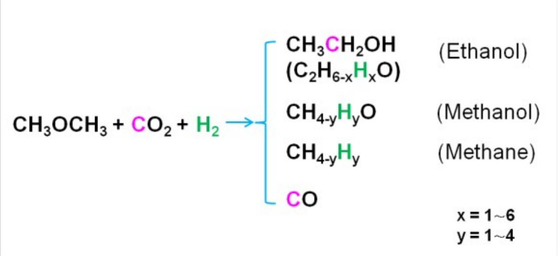
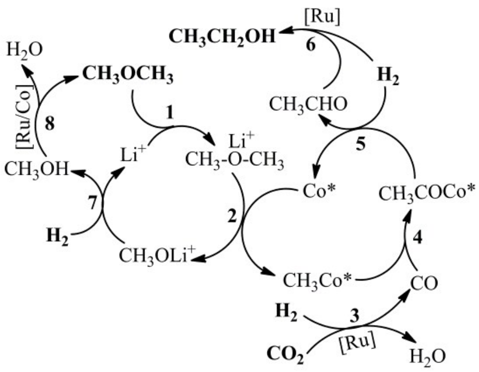


Figure 4. The origin of C and H atoms in the reaction products.



Scheme 2. The proposed mechanism of the reaction.

The Lewis acid promoted methyl Co complex formation has been reported elsewhere.[28] CO was generated in situ via RWGS reaction, promoted by Ru catalyst (Step **3**, Figure S16). The Ru catalyzed RWGS reaction has been studied elsewhere.[29] Then the CO inserted into the CH_3-Co* bond, resulting in the CH_3COCo* complex (Step **4,** Figure S9) The insertion of CO into metal-carbon bond is a basic step in organic chemistry.[25] In the presence of H_2, acetaldehyde was formed via reductive elimination of the acetyl group (Step **5,** Figure S17). The acetaldehyde was readily reduced into ethanol product by H_2, promoted by Ru catalyst (Step **6**, Figure S18). The other moiety of DME generated in Step 2 was transformed into methanol (Step **7**), which could be supported by the existence of methanol byproduct (Figure S1). The methanol formed was converted in situ into DME by Ru and/or Co catalysts and started the new reaction cycles (Step **8**, Figure S19).

The excellent catalytic results may be attributed to the synergy of the above catalytic cycles. Among these cycles, the rate of the RWGS reaction to form CO was critical to the reaction result. If the catalytic activity of the RWGS reaction was too low the ethanol formation rate would certainly be low. But when the CO concentration in the reaction was high enough, little ethanol was detected, and considerable acetate esters and/or acetic acid emerged (Figures S20 and S21). The methyl acetate can be produced via DME carbonylation, catalyzed by Co catalyst (Figure S22). The acetyl group, formed in Step 4, increased with the elevating CO content. If the CO concentration was high, acetyl group could be converted into methyl acetate with the CH_3O, generated in Step 2, before its hydrogenation took place. The detailed mechanism of DME carbonylation has been reported in the literature.[30] The ethyl acetate and/or acetic acid were produced via further transformation of methyl acetate with CO and/or H_2.[25] In this work, ethanol was the predominant product, and no acetate or acetic acid were observed. This is mainly because the rate of the RWGS reaction was appropriate. Interestingly, in this work the Co catalyzed DME carbonylation to synthesize methyl acetate could proceed reversely at reaction conditions (Figure S23), inhibiting the methyl acetate formation and its further conversion. In the reported DME hydrocarbonylation using syngas (CO/H_2), whether by heterogeneous or homogeneous catalysts, methanol was usually the major product.[26,28] While in this work, the methanol generated in situ was directly recycled to DME, which accounts for the very low level of methanol during the reaction. It is known that Ru complex can promote the hydrogenation of CO_2/CO into methanol and/or methane.[6c] Whereas in this work the amount of methanol and methane produced from the CO_2/CO hydrogenation were hardly detectable (Figures S2b and S8b).

Conclusions

In summary, we have developed a route of ethanol synthesis from DME, CO_2 and H_2. The reaction can be effectively catalyzed by Ru-Co bimetallic catalyst. Ethanol can be produced at above 150 °C. The catalytic activity can be as high as 132.5 C-mmol $L^{-1}h^{-1}$ at 180 °C. The selectivity of ethanol in total products can reach 71.7 C-mol%, and the selectivity of ethanol in liquid product could reach 94.1%. In addition, the catalyst can be reused at least 5 times without obvious change of catalytic performance. The very high efficiency of the reaction resulted from several reasons. Firstly, the DME (not via methanol or methyl iodide) directly took part in the formation of ethanol, reducing the methane byproduct. Secondly, the methanol produced can be in situ recycled to DME feedstock, and thus the selectivity to ethanol is enhanced. Finally, the Ru and Co cooperate very well to accelerate the desired reaction. The strategy opens a new way of ethanol synthesis and CO_2 transformation. We believe that some other value-added chemicals can also be synthesized using DME and CO_2 as the starting materials.

Experimental

Chemicals. Ruthenium carbonyl ($Ru_3(CO)_{12}$, >98%) and Tris(Triphenylphosphine)ruthenium(II) dichloride ($Ru(PPh_3)_3Cl_2$, 99%), ruthenium acetylacetonate ($Ru(acac)_3$, 98+%) were purchased from Adamas Reagent, Ltd. Tetracarbonyl di-u-chlorodirhodium(I) ($Rh_2(CO)_4Cl_2$, Rh 50.1-52.9%), anhydrous lithium iodide (LiI, 99.95%), potassium iodide (KI, 99.9%), lithium tetrafluoroborate ($LiBF_4$, 98%), cobalt(II) iodide (CoI_2, 99.5%), ferrocene (99%), decacarbonyl dimanganese ($Mn_2(CO)_{10}$, C 30.6%) and 2-pyrrolidinone (99%) were obtained from Alfa Aesar China Co, Ltd. Zinc iodide (ZnI_2, 98%), nickel(II) chloride ($NiCl_2$, 98%), formaldehyde (HCHO, analytical grade, 40% solution in H_2O) and N-methylpyrrolidine (98%) were

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provided by J&K Chemical Ltd. (Shanghai). 1,3-Dimethyl-2-imidazolidinone (DMI, 99%), dicobalt octacarbonyl ($Co_2(CO)_8$), lithium chloride (LiCl, 98%) and benzene (99.5%) were purchased from TCI Shanghai Co, Ltd. Formic acid (HCOOH, 88% solution in H_2O), N-methyl-2-pyrrolidone (NMP, 99.5%), N,N-dimethylformamide (DMF, 99.5%) and cyclohexane (99.5%) were provided by Sinopharm Chemical Reagent Co., Ltd. Methanol (99.5%), acetic acid (99.5%) and cyclohexanone (99.5%) were obtained from Beijing Chemical Company. Toluene (99.8%, HPLC) was obtained from Xilong Chemical Co., Ltd. Iridium carbonyl ($Ir_4(CO)_{12}$, 98+%), copper(II) sulfate ($CuSO_4$, 98%) and acetaldehyde (CH_3CHO, 99.5%) were purchased from Acros Organics. Methyl iodide (CH_3I, 99%) was bought from Shandong Xiya Chemical Industry Co., Ltd. Dimethyl ether (DME, 99.9%) was obtained from Zhao Qing Gao Neng Da Chemical Industry Co., Ltd. Deuterium gas (D_2, 99.999%) was offered by Zhengzhou Xingdao Chemical Technology Co., Ltd. The CO_2 (99.99%), H_2 (99.99%) and CO (99.99%) were provided by Beijing Analytical Instrument Company.

Catalytic reaction. The apparatus and procedures were similar to our previous work.[5a] All the reactions were conducted in a 16 mL Teflon-lined stainless steel batch reactor equipped with a magnetic stirrer. The inner diameter of the reactor was 18 mm. In a typical experiment, known amounts of Ru and/or Co catalysts, LiI or another promoter, and 2 mL DMI or another solvent were loaded sequentially into the reactor. The reactor was filled with DME of saturated vapor pressure (0.5 MPa) at room temperature after the reactor was purged three times with the same gas. Then CO_2 in the cylinder was charged into the reactor to desired pressure, and the inlet valve of CO_2 was closed. Then H_2 was charged into the reactor until suitable total pressure was reached. The reactor was placed in an air bath of constant temperature, and the magnetic stirrer was started at 800 rpm. After reaction, the reactor was cooled in an ice-water bath for 1 h, the residual gas was released slowly and collected in a gasbag. The liquid mixture was analyzed by GC (Agilent 7890B) equipped with a flame ionization detector and an HP-5 capillary column (0.32 mm in diameter, 30 m in length) using toluene as the internal standard. Identification of the liquid products was done using a GC-MS (Agilent-7890B-5977A) as well as by comparing the retention times of the standards in the GC traces. The yields of the products were calculated from the GC data. NMR spectra were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz). The gaseous samples were analyzed using a GC (Agilent 4890D) equipped with a TCD detector and a packed column (Carbon molecular sieve TDX-01, 3 mm in diameter and 1 m in length) using Argon as the carry gas.

Recycling test. After reaction, the reactor was cooled down in an ice bath after reaction and the residual gas was released. The amount of product was determined as discussed above. Then the alcohols formed and unreacted DME in the reactor were removed in a vacuum oven at 80 °C for 3 h, which was confirmed GC analysis. The catalytic system was used directly for the next run.

Conflicts of interest

There are no conflicts of interest to declare.

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References

1 J. Goldemberg, Science, 2007, **315**, 808-810.

2 X. G. San, Y. Zhang, W. J. Shen and N. Tsubaki, *Energy & Fuels,* 2009, **23**, 2843-2844.

3 M. Aresta, Carbon Dioxide as Chemical Feedstock, (Wiley–VCH, Weinheim, 2010).

4 (a) M. Y. He, Y. H. Sun and B. X. Han, *Angew. Chem. Int. Ed*., 2013, **52**, 9620-9633; (b) J. Klankermayer, S. Wesselbaum, K. Beydoun and W. Leitner, *Angew. Chem. Int. Ed*., 2016, **55**, 7296-7343; (c) W. Wang, S. P. Wang, X. B. Ma and J. L. Gong, *Chem. Soc. Rev*., 2011, **40**, 3703-3727; (d) P. G. Jessop, F. Joóand C. C. Tai, *Coord. Chem. Rev*., 2004, **248**, 2425-2442; (e) Q. Liu, L. P. Wu, R. Jackstell and M. Beller, *Nat. Commun*., 2015, **6**, 5933.

5 (a) Q. L. Qian, J. J. Zhang, M. Cui and B. X. Han, *Nat. Commun*., 2016, **7**, 11481; (b) J. Wei, Q. J. Ge, R. W. Yao, Z. Y. Wen, C. Y. Fang, L. S. Guo, H. Y. Xu and J. Sun, *Nat. Commun*., 2017, **8**, 15174; (c) Y. Liu, W. M. Ren, J. Liu and X. B. Lu, *Angew. Chem. Int. Ed*., 2013, **52**, 11594 – 11598; (d) M. Cui, Q. L. Qian, J. J. Zhang, C. J. Chen and B. X. Han, *Green Chem.*, 2017, **19**, 3558–3565; (e) C. Liu, J. H. Xie, G. L. Tian, W. Li and Q. L. Zhou, *Chem. Sci*., 2015, **6**, 2928-2931; (f) Q. W. Song, Z. H. Zhou and L. N. He, *Green Chem.*, 2017, **19**, 3707-3728; (g) F. Ferretti, M. Sharif, S. Dastgir, F. Ragaini, R. Jackstell and M. Beller, *Green Chem*., 2017, **19**, 3542-3548; (h) J. Wang, Z. Hao and S. Wohlrab, *Green Chem*., 2017, **19**, 3595-3600; (i) T. V. Q. Nguyen, J. A. Rodríguez-Santamaría, W. Yoo and S. Kobayashi, *Green Chem*., 2017, **19**, 2501-2505.

6 (a) S. Kattel, P. J. Ramírez, J. G. Chen, J. A. Rodriguez and P. Liu, *Science,* 2017, **355**, 1296-1299; (b) J. Graciani, K. Mudiyanselage, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz and J. A. Rodriguez, *Science,* 2014, **345**, 546-550; (c) S. Wesselbaum, T. V. Stein, J. Klankermayer and W. Leitner, *Angew. Chem. Int. Ed*., 2012, **51**, 7499-7502; (d) Z. B. Han, L. C. Rong, J. Wu, L. Zhang, Z. Wang and K. L. Ding, *Angew. Chem. Int. Ed*., 2012, **51**, 13041-13045; (e) H. Yang, S. Qin, H. Wang and J. Lu, *Green Chem*., 2015, **17**, 5144-5148; (f) J. Albo, M. Alvarez-Guerra, P. Castaño and A. Irabien, *Green Chem*., 2015, **17**, 2304-2324; (g) F. Liao, X. Wu, J. Zheng, M. M. Li, A. Kroner, Z. Zeng, X. Hong, Y. Yuan, X. Gong and S. C. E. Tsang, *Green Chem*., 2017, **19**, 270-280.

7 H. Kusama, K. Okabe, K. Sayama and H. Arakawa, *Energy,* 1997, **22**, 343-348.

8 K. K. Bando, K. Soga, K. Kunimori, H. Arakawa, *Appl. Catal. A-Gen*., 1998, **175**, 67-81.

9 H. Kurakata, Y. Izumi and K. Aika, *Chem. Commun*., 1996, 389-390.

View Article Online
DOI: 10.1039/C7GC02807E

10 T. Inui and T. Yamamoto, *Catal. Today,* 1998, **45**, 209-214.

11 T. Inui, T. Yamamoto, M. Inoue, H. Hara, T. Takeguchi and J. B. Kim, *Appl. Catal. A-Gen*., 1999, **186**, 395-406.

12 L. S. Davy, D. Nieskens, Y. Ferrari, R. Liu and J. Kolonko, *Catal. Comm*., 2011, **14**, 111-113.

13 S. G. Li, H. J. Guo, C. R. Luo, H. R. Zhang, L. Xiong, X. D. Chen and L. L. Ma, *Chem. Lett.,* 2013, **143**, 345-355.

14 M. Cui, Q. L. Qian, Z. H. He, Z. F. Zhang, J. Ma, T. B. Wu, G. Y. Yang and B. X. Han, *Chem. Sci*., 2016, **7**, 5200-5205.

15 Q. L. Qian, M. Cui, Z. H. He, C. Y. Wu, Q. G. Zhu, Z. F. Zhang, J. Ma, G. Y. Yang, J. J. Zhang and B. X. Han, *Chem. Sci*., 2015, **6**, 5685-5689.

16 K. Tominaga, Y. SaSaki, M. Saito, K. Hagihara and T. Watanabe, *J. Mol. Catal.,* 1994, **89**, 51-56.

17 Z. H. He, Q. L. Qian, J. Ma, Q. L. Meng, H. C. Zhou, J. L. Song, Z. M. Liu and B. X. Han, *Angew. Chem. Int. Ed*., 2016, **55**, 737-741.

18 (a) K. Tominaga, Y. Sasaki, T. Watanabe and M. Saito, *Stud. Surf. Sci. Catal*., 1998, **114**, 495-498; (b) J. J. Zhang, Q. L. Qian, M. Cui, C. J. Chen, S. S. Liu, B. X. Han, *Green Chem*., 2017, **19**, 4396-4401.

19 (a) M. Beller and U. T. Bornscheuer, *Angew. Chem. Int. Ed*., 2014, **53**, 4527-4528; (b) G. Prieto, *ChemSusChem,* 2017, **10**, 1056-1070.

20 S. X. Bai, Q. Shao, P. T. Wang, Q. G. Dai, X. Y. Wang and X. Q. Huang, *J. Am. Chem. Soc*., 2017, **139**, 6827-6830

21 (a) B. R. Sohnlein, S. G. Li, J. F. Fuller and D. S. Yang. *J. Chem. Phys*., 2005, **123**, 014318; (b) S. E. Hill, E. D. Glendening and D. Feller, *J. Phys. Chem. A,* 1997, **101**, 6125-6131.

22 P. M. Maitlis, A. Haynes, B. R. James, M. Catellani and G. P. Chiusoli, *Dalton Trans*., 2004, 3409-3419.

23 S. D. Badmaev, V. D. Belyaev, G. G. Volkova, E. A. Paukshtis and V. A. Sobyanin, *React. Kinet. Catal. Lett.,* 2007, **90**, 197-204.

24 M. Roper and H. Loevenich, *J. Organomet. Chem*., 1983, **255**, 95-102.

25 (a) G. Braca, S G. brana, G. Valentini, G. Andrich and G. Gregorio, *J. Am. Chem. Soc*., 1978, **100**, 6238-6240; (b) G. Braca, L. Paladini, G. Sbrana, G. Valentini, G. Andrich and G. Gregorio, *Ind. Eng. Chem. Prod. Res. Dev*., 1981, **20**, 115-122.

26 (a) P. Lu, G. H. Yang, Y. Tanaka and N. Tsubaki, *Catal. Today,* 2014, **232**, 22-26; (b) D. Wang, G. H. Yang, Q. X. Ma, Y. Yoneyama, Y. S. Tan, Y. Z. Han and N. Tsubaki, *Fue*l, 2013, **109** , 54-60.

27 T. Junk and W. J. Catallo, *Chem. Soc. Rev*., 1997, **26**, 401-406.

28 R. Bartek, M. M. Habib and W. R. Pretzer, *J. Mol. Catal*., 1985, **33**, 245-248.

29 K. Tsuchiya, J. Huang and K. Tominaga, *ACS Catal*., 2013, **3**, 2865-2868.

30 (a) D. B. Rasmussen, J. M. Christensen, B. Temel, F. Studt, P. G. Moses, J. Rossmeisl, A. Riisager and A. D. Jensen, *Angew. Chem. Int. Ed*., 2015, **54**, 7261-7264; (b) P. Cheung, A. Bhan, G. J. Sunley and E. Iglesia, *Angew. Chem. Int. Ed*., 2006, **45**, 1617-1620.