Green Chemistry

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c7gc01887h

Synthesis of ethanol from paraformaldehyde, CO_2 and H_2†

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Received 23rd June 2017,
Accepted 7th August 2017

DOI: 10.1039/c7gc01887h

rsc.li/greenchem

Ethanol is an important bulk chemical and alternative fuel that is currently synthesized by catalytic hydration of ethylene or fermentation of foods. CO_2 is a cheap and renewable carbon resource. Transformation of CO_2 into useful chemicals is an interesting topic in green chemistry. Production of ethanol using CO_2 and H_2 is a promising route, but the efficiency of the reaction is not satisfactory. In this paper, we propose a protocol to synthesize ethanol from paraformaldehyde, CO_2 and H_2. The reaction could be efficiently accelerated by a Ru–Co bimetallic catalyst using LiI as the promoter in 1,3-dimethyl-2-imidazolidinone (DMI) under mild conditions. The selectivity of ethanol in total products reached 50.9 C-mol%, which was obviously higher than that of the reported routes. Furthermore, the TOF of ethanol based on Ru metal was as high as 17.9 h^{-1}. To our knowledge, this is the first report on ethanol synthesis from paraformaldehyde, CO_2 and H_2. A detailed study indicated that the outstanding results of the reaction originated from the synergy of paraformaldehyde hydrogenation, reverse water gas shift reaction and methanol homologation.

Introduction

As an important bulk chemical, ethanol is widely used as a solvent, food, medicine, pesticide, organic feedstock, *etc.* Moreover, ethanol has played an ever-increasing role in the current energy infrastructure.[1] Nowadays, ethanol is mainly manufactured by catalytic hydration of ethylene from petroleum or fermentation of foods such as corn and sugarcane. CO_2 is the major greenhouse gas. It is also an economical, safe, renewable and readily available carbon resource.[2] Transforming CO_2 into useful chemicals has received much attention from the scientific community. So far, CO_2 has been utilized to synthesize a variety of products, such as carboxylic acids, esters, carbonates, urea, formamides, hydrocarbons and alcohols.[3] As for alcohols, significant progress has been made in methanol synthesis *via* CO_2 hydrogenation in the past few decades.[4] Synthesis of ethanol using CO_2 and H_2 as feedstock is obviously of great importance. But it is still a great challenge because it involves CO_2 hydrogenation with simultaneous C–C bond formation.[5]

The reports of ethanol synthesis using CO_2 were mostly limited to CO_2 hydrogenation at high temperatures.[6–12] In such routes, CO_2 usually reacted with H_2 to generate reactive C_1 intermediates, including CO, CH_3* and/or CH_3OH, and the intermediates underwent the C–C bond formation step to produce C_{2+} products, such as ethanol and higher alcohols.[6,7] Because the *in situ* generation of C_1 intermediates from CO_2 hydrogenation and the carbon chain growth took place simultaneously, the product distribution was usually broad and the selectivity of ethanol in the alcohols and/or total products was generally low. For example, in the CoMoS catalyzed CO_2 hydrogenation the best result was obtained at 340 °C.[10] The mixed alcohols were produced and methanol was the predominant alcohol (20.0 C-mol%), while ethanol selectivity was only 5.5 C-mol% in the total products. When CO_2 hydrogenation was catalyzed by K/Cu–Zn at 300 °C, C_1–C_5 alcohols were formed and the ethanol selectivity in the total products was merely 19.5 wt%.[11] In the Pt/Co_3O_4 catalyzed synthesis of higher alcohols from CO_2 hydrogenation, C_1–C_4 alcohols were produced and the ethanol selectivity in the total products was also low (18.9 C-mol%).[12] To improve the ethanol selectivity, introducing certain substrates to react with CO_2 and H_2 is a viable way. When methanol, CO_2 and H_2 were used as the starting materials, ethanol was the only alcohol product and the ethanol selectivity in the total products reached 34.2 C-mol%.[13] In addition, the yield of ethanol based on methanol was 32% and the highest TOF of ethanol based on Ru metal was only 1.1 h^{-1}. At the present stage, methanol was

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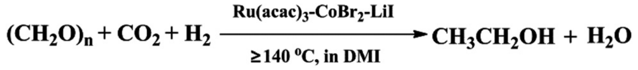
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7gc01887h



$$(CH_2O)_n + CO_2 + H_2 \xrightarrow[\geq 140\ ^{o}C,\ in\ DMI]{Ru(acac)_3\text{-}CoBr_2\text{-}LiI} CH_3CH_2OH + H_2O$$

Scheme 1 Synthesis of ethanol from paraformaldehyde, CO_2 and H_2.

the only substrate reported to react with CO_2 and H_2 for the synthesis of ethanol. Exploration of the route for ethanol synthesis by reaction of other substrates with CO_2 and H_2 is interesting from both scientific and practical perspectives.

Formaldehyde is a bulk chemical that can be produced by various routes, such as CO_2 hydrogenation, methane and/or methanol oxidation.[14–16] Paraformaldehyde, which can be easily derived from formaldehyde, is a facile source of formaldehyde that is preferred especially when anhydrous conditions are required.[17] Herein we report the synthesis of ethanol from paraformaldehyde, CO_2 and H_2 (Scheme 1). The reaction could proceed very efficiently by homogeneous catalysis under mild conditions. To the best of our knowledge, this is the first report on the synthesis of ethanol from aldehyde, CO_2 and H_2.

Results and discussion

The reaction was effectively catalyzed by the Ru–Co bimetallic catalyst using LiI as the promoter in 1,3-dimethyl-2-imidazolidinone (DMI) solvent under milder conditions, as shown in Table 1. Ethanol was the predominant product in the reaction solution (Fig. S1 and S2†). The yield of ethanol based on the "CH_2O" monomer in paraformaldehyde was 37.8%. Only small amounts of CO and methane were generated, and the ethanol selectivity in the total products reached 50.9 C-mol%, which is superior to that of reported methanol homologation using CO_2 and H_2.[13] Interestingly, the TOF of ethanol based on Ru metal was as high as 17.9 h^{-1} (entry 1), which is much higher than that of the reported routes.[9,13]

Table 1 Different catalytic systems of ethanol synthesis from paraformaldehyde, CO_2 and H_2[a]

Entry	Catalyst	Promoter	Solvent	TOF[b] (h^{-1})
1[c]	$Ru(acac)_3$, $CoBr_2$	LiI	DMI	17.9
2[d]	$Fe(acac)_3$, $CoBr_2$	LiI	DMI	0.3
3[d]	$Mn(acac)_3$, $CoBr_2$	LiI	DMI	0.2
4[d]	$Ni(acac)_2$, $CoBr_2$	LiI	DMI	0
5	$Ru(acac)_3$, $CuBr_2$	LiI	DMI	0.2
6	$Ru(acac)_3$, $NiBr_2$	LiI	DMI	0
7[d]	$Rh_6(CO)_{16}$, $Fe_2(CO)_9$	LiI	DMI	0
8[d]	$Ir(OAc)_n$, $NiBr_2$	LiI	DMI	0
9	$Ru(acac)_3$	LiI	DMI	1.2
10[d]	$CoBr_2$	LiI	DMI	0
11	$Ru(acac)_3$, CoI_2	LiI	DMI	13.4
12	$Ru_3(CO)_{12}$, $CoBr_2$	LiI	DMI	13.6
13[d]	$RuBr_3$, CoI_2	LiI	DMI	9.0
14[d]	$RuCl_3$, $CoCl_2$	LiI	DMI	11.6
15	$Ru(PPh_3)_3Cl_2$, $Co(PPh)_3Cl$	LiI	DMI	14.7
16	$Ru(acac)_3$, $CoBr_2$	—	DMI	0
17	$Ru(acac)_3$, $CoBr_2$	LiCl	DMI	7.5
18	$Ru(acac)_3$, $CoBr_2$	LiBr	DMI	7.7
19[d]	$Ru(acac)_3$, $CoBr_2$	$LiBF_4$	DMI	0
20[d]	$Ru(acac)_3$, $CoBr_2$	I_2	DMI	0
21	$Ru(acac)_3$, $CoBr_2$	NaI	DMI	13.4
22	$Ru(acac)_3$, $CoBr_2$	KI	DMI	9.6
23[d]	$Ru(acac)_3$, $CoBr_2$	ZnI_2	DMI	0.1
24[d]	$Ru(acac)_3$, $CoBr_2$	MgI_2	DMI	0
25[d]	$Ru(acac)_3$, $CoBr_2$	CaI_2	DMI	0
26[d]	$Ru(acac)_3$, $CoBr_2$	CuI	DMI	0
27	$Ru(acac)_3$, $CoBr_2$	LiI	NMP	11.3
28[d]	$Ru(acac)_3$, $CoBr_2$	LiI	THF	0
29	$Ru(acac)_3$, $CoBr_2$	LiI	DMF	0
30	$Ru(acac)_3$, $CoBr_2$	LiI	Water	0
31[d]	$Ru(acac)_3$, $CoBr_2$	LiI	Cyclohexane	0

[a] Reaction conditions: 7.5 μmol Ru catalyst and 45 μmol Co catalyst (based on the metal), 3 mmol promoter, 2 mL solvent, 0.1 g $(CH_2O)_n$ (*i.e.*, 3.2 mmol "CH_2O" monomer), 3 MPa CO_2 and 5 MPa H_2 (at room temperature), 180 °C, 9 h. [b] TOF denotes moles of ethanol produced per mole of Ru catalyst per hour. [c] The yield of ethanol based on the "CH_2O" monomer in paraformaldehyde was 37.8% and ethanol selectivity in the total products reached 50.3 C-mol% (the product distribution: ethanol 1.21 mmol, methanol 0.12 mmol, propanol 0.05 mmol, CO 1.11 mmol, and methane 0.95 mmol). [d] Precipitate was observed after the reaction.

The Ru–Co bimetallic catalyst is crucial for the target reaction. When the $Ru(acac)_3$ catalyst was replaced with other commonly used transition metal complexes, *i.e.*, Fe, Mn, and Ni, the reaction rates were very low or the reaction did not take place (entries 2–4). When $Ru(acac)_3$ was fixed and $CoBr_2$ was replaced with other metal complexes (Cu, Ni), the results were also poor (entries 5 and 6). When we tried other combinations of metal complexes (Rh/Fe, Ir/Ni), no ethanol was produced after the reaction (entries 7 and 8). Thus Ru–Co was the suitable combination of catalysts for the reaction. When we used $Ru(acac)_3$ or $CoBr_2$ separately, the results revealed that the Ru complex was the major catalyst and the Co complex was the cocatalyst (entries 9 and 10). The activity of the Ru catalyst was greatly enhanced by the Co cocatalyst, indicating a synergic effect between the Ru and Co complexes (entries 1 and 9). After screening the combinations of Ru and Co complexes, it was found that $Ru(acac)_3/CoBr_2$ exhibited better performance in accelerating the reaction (entries 1 and 11–15).

The promoter was also important for the reaction. Without the promoter, no ethanol was observed (entry 16). If the I^- of LiI was replaced with other halogen anions (Cl^-, Br^-), the reaction proceeded at much lower rates (entries 17 and 18). We also tried $LiBF_4$, but no ethanol was generated (entry 19). When we used I_2 as the promoter the reaction did not take place (entry 20). Thus, the ionic state of the halogen was needed as a promoter and I^- was the best choice. The I^- helped to maintain the catalyst stability (entries 1 and 19). In addition, the larger size of iodide compared with other halides has a stronger steric effect, leading to better catalytic selectivity (entries 1, 17 and 18).[18] The metal cation of the iodide promoter also greatly affected the catalytic performance. The alkali metal (Li, Na, K) iodides were effective promoters, and the LiI displayed the best catalytic performance (entries 1, 21 and 22), due to its stronger Lewis acidity and better solubility in the reaction solution.[7,13] However, the ethanol formation rate was very low or the reaction did not proceed when other metal iodides (ZnI_2, MgI_2, CaI_2, CuI) were utilized (entries 23–26). The reason may result from their poor solubility in the reaction solvent. We also screened the reaction solvent, such as NMP, THF, DMF, water and cyclohexane, and the results indicated that DMI was the suitable solvent for the reaction (entries 27–31). In brief, the catalytic system consisting of Ru(acac)$_3$, CoBr$_2$, LiI and DMI was appropriate for the target reaction.

Fig. 1 showed the impact of temperature on the catalytic activity. The reaction did not take place at 120 °C, and obvious ethanol was observed at 140 °C. The reaction rate increased remarkably with the increase of temperature until 180 °C. At this temperature the TOF of ethanol reached 17.9 h^{-1}. After 180 °C, the catalytic activity had little elevation with the temperature rise. So, 180 °C is suitable for this reaction.

Based on the optimization of the reaction temperature as above, we further studied the influence of other reaction parameters, such as pressure and dosage of the catalyst components, as revealed in Table 2. At a fixed ratio of CO_2 and H_2 (3/5), the ethanol formation rate increased evidently with the increasing total pressure (entries 1–4). However, the effect of total pressure was not obvious at >8 MPa (entry 5). When the total pressure of CO_2 and H_2 was fixed at 8 MPa, the best catalytic performance was also obtained at 3 MPa CO_2 and 5 MPa H_2 (entries 4 and 6–9). Both CO_2 and H_2 were necessary for the reaction, because no or little ethanol was produced without CO_2 and/or H_2 (entries 10–12). Interestingly, a small amount of ethanol could be observed when paraformaldehyde reacted with H_2 under reaction conditions (entry 12), which may be due to the small amount of CO generated *in situ via* partial decomposition of paraformaldehyde.[19] Paraformaldehyde was also necessary for the target reaction. Without this substrate, only trace ethanol was detected after the reaction (TOF = 0.2 h^{-1}) (entry 13). The ethanol synthesis *via* Ru–Co catalyzed CO_2 hydrogenation has been reported in the literature, where the catalytic rates were also low (TOF < 0.8 h^{-1} based on Ru metal, at 200 °C).[9] Thus the introduction of the paraformaldehyde not only markedly improved the ethanol selectivity, but also greatly enhanced the reaction rate. When the substrates of different polymerization degrees were used to react with CO_2 and H_2, respectively, ethanol was produced at similar rates (entries 4 and 14). These results indicate that the synthesis route in this work can be applied to paraformaldehydes from different sources.

Table 2 Effect of reaction parameters on the reaction[a]

Entry	Ru (μmol)	Co (μmol)	LiI (mmol)	CO_2/H_2 (MPa)	TOF (h^{-1})
1	7.5	45	3	0.75/1.25	5.0
2	7.5	45	3	1.5/2.5	10.6
3	7.5	45	3	2.25/3.75	14.1
4	7.5	45	3	3/5	17.9
5	7.5	45	3	3.75/6.25	18.7
6	7.5	45	3	1/7	13.6
7	7.5	45	3	2/6	15.5
8	7.5	45	3	4/4	12.8
9	7.5	45	3	5/3	8.9
10	7.5	45	3	0/0	0
11	7.5	45	3	3/0	0
12	7.5	45	3	0/5	1.2
13[b]	7.5	45	3	3/5	0.2
14[c]	7.5	45	3	3/5	15.6
15	7.5	45	2	3/5	14.8
16	7.5	45	4	3/5	8.4
17	5	30	3	3/5	16.4
18	10	60	3	3/5	13.7
19	5	47.5	3	3/5	15.2
20	15	37.5	3	3/5	7.8
21	22.5	30	3	3/5	5.8
22	45	7.5	3	3/5	0.4

[a] Reaction conditions: Ru(acac)$_3$ and CoBr$_2$ were used as catalyst precursors; 2 mL DMI, 3.2 mmol "CH_2O" monomer (0.1 g), 180 °C, 9 h. [b] No $(CH_2O)_n$ was added before the reaction. [c] 1,3,5-Trioxane (3.2 mmol "CH_2O" monomer, 0.1 g) was used instead of $(CH_2O)_n$.

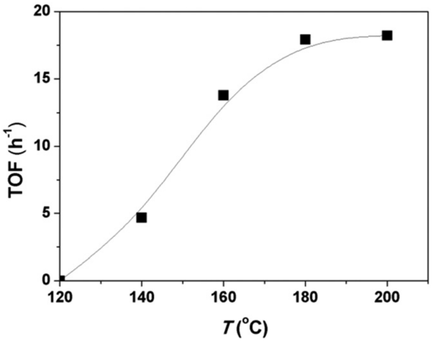


Fig. 1 The TOF of ethanol at different temperatures. Reaction conditions: 7.5 μmol Ru(acac)$_3$ and 45 μmol CoBr$_2$, 3 mmol LiI, 2 mL DMI, 3.2 mmol "CH_2O" monomer (0.1 g), 3 MPa CO_2 and 5 MPa H_2 (at room temperature), 9 h.

The dosage of LiI may affect the catalytic properties and 3 mmol LiI in the catalytic system resulted in high efficiency (entries 4, 15 and 16). Iodide anions are not only good nucleophiles but also good ligands for transition metals. Hence, suitable amounts of LiI were necessary for the reaction, while too much of it would occupy the active sites of the catalyst, inhibiting the reaction.[18] The dosages of the Ru and Co catalysts also evidently influenced the reaction. At the fixed proportion of Ru and Co metals (1/6), the combination of 7.5 μmol Ru and 45 μmol Co gave the highest catalytic activity (entries 4, 17 and 18). When the total amount of Ru and Co catalysts was kept at 52.5 μmol, the best ratio of Ru and Co catalysts was also 1/6 (entries 4 and 19–22).

Under the optimized conditions, we tested the reusability of the catalytic system (Ru(acac)$_3$/CoBr$_2$-LiI-DMI). After the reaction, the alcohols produced in the reaction were removed under vacuum at 85 °C for 5 h, which was proved by GC analysis. Then the catalytic system was used directly for the next run. The results demonstrated that the catalytic system could be recycled at least five times without obvious loss of activity and the TON of ethanol reached 805 in the five cycles (Fig. 2).

Fig. 3 depicts the time course of the alcohol formation. The paraformaldehyde was quickly transformed into methanol at the initial period of the reaction. After 1 h ethanol began to emerge and it grew steadily until 9 h. Accordingly, methanol generated at the beginning decreased continuously with the increase of the ethanol amount, suggesting that ethanol was

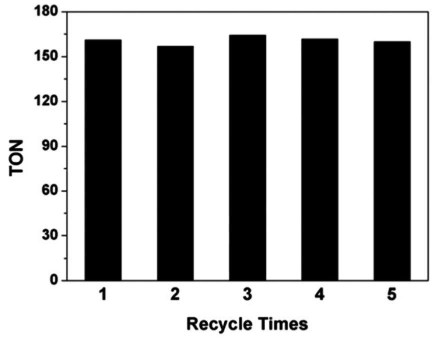


Fig. 2 The results of the recycling tests. Reaction conditions: 7.5 μmol $Ru(acac)_3$ and 45 μmol $CoBr_2$, 3 mmol LiI, 2 mL DMI, 3.2 mmol "CH_2O" monomer (0.1 g), 3 MPa CO_2 and 5 MPa H_2 (at room temperature), 180 °C, 9 h. TON denotes moles of ethanol produced per mole of Ru catalyst.

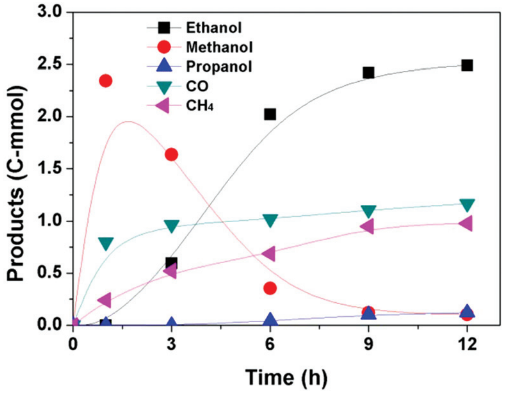
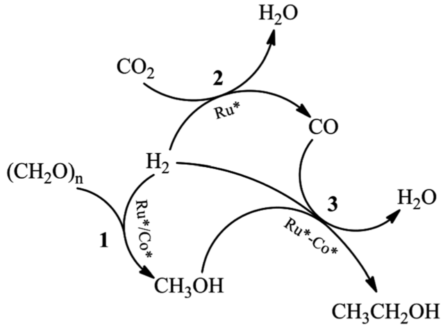


Fig. 3 Time course of the reaction. Reaction conditions: 7.5 μmol $Ru(acac)_3$ and 45 μmol $CoBr_2$ (based on the metal), 3 mmol LiI, 2 mL DMI, 3.2 mmol "CH_2O" monomer (0.1 g), 3 MPa CO_2 and 5 MPa H_2 (at room temperature), and 180 °C.



Scheme 2 The synergy of the reactions for ethanol synthesis from paraformaldehyde, CO_2 and H_2. Ru* and Co* represent the active species of Ru and Co, respectively.

formed *via* the methanol homologation pathway. After 9 h, the reaction rate became much lower because methanol was nearly used up. Moreover, trace propanol could be detected at 6 h and it grew slowly with time. As for the gaseous products, CO was produced at the start of the reaction and its content was nearly kept constant in the reaction process, indicating the fast consumption of CO in the subsequent steps. However, in the literature the CO content increased evidently at the initial period of the reaction and dropped continuously with time.[13,9b] Methane was observed when the reaction began and it increased gradually during the reaction.

From the above results, we can deduce that synthesis of ethanol from paraformaldehyde, CO_2 and H_2 is the synergy of three basic reactions (Scheme 2), *i.e.*, hydrogenation of paraformaldehyde to methanol (**1**), reverse water gas shift reaction (RWGS) (**2**), and methanol homologation (**3**). The GC-MS and NMR spectra of tracer experiments using $(^{13}CH_2O)_n$ indicated that the ^{13}C atoms were transformed into alcohols, *i.e.*, $^{13}CH_3OH$ and $^{13}CH_3CH_2OH$, supporting the above argument (Fig. S3 and S4†). A small amount of propanol was generated by the homologation of ethanol. The results obtained using $(CD_2O)_n$ indicated that H/D exchange took place in the reaction (Fig. S5†). Most of the D atoms on $(CD_2O)_n$ entered the methanol molecules (CD_2H_2O), and H/D exchange was observed because a small amount of CD_3HO was observed after the reaction. Then the major D atoms on methanol were further replaced by the H atoms of H_2 during the formation of ethanol, because only a small amount of $C_2D_2H_4O$ was detected. The results using D_2 also demonstrated a similar exchange process (Fig. S6†). The H–D exchange was also studied for other reactions.[20]

The hydrogenation of paraformaldehyde to methanol could be promoted by the Ru or Co catalyst, respectively (Fig. S7 and S8†). The hydrogenation of paraformaldehyde to methanol is a well-known reaction.[21] The RWGS reaction could be catalyzed by the Ru catalyst (Fig. S9†). The Ru promoted RWGS reaction has been studied by other researchers.[22] Methanol homologation into ethanol could be accelerated by a Ru–Co bimetallic catalyst (Fig. S10†). The Ru–Co catalyzed methanol homologation has also been investigated in the literature.[23] The high catalytic rate and selectivity of this work lie in not only the synergy of the cascade reactions but also the synergy of different catalytic components. The presence of a small amount of the propanol product revealed that the catalytic system has strong capability for promoting alcohol homologation, while no higher alcohol was observed in ethanol synthesis from methanol, CO_2 and H_2 reported in the literature.[13] The very high rate of paraformaldehyde hydrogenation and methanol homologation caused the quick consumption of CO generated by the RWGS reaction, resulting in a high ethanol formation rate with less CO byproduct. The catalytic rate of the RWGS process was also crucial to the reaction (Fig. S11†). If the CO formation rate was too low the ethanol generation would certainly be depressed, whereas the ethanol formation was also inhibited when the CO content was high enough during the reaction. This could be attributed to the poisoning of the catalyst by excess CO.[3e] Furthermore, only a small amount of methane was detected in CO_2/CO hydrogenation promoted by the catalytic system (Fig. S12–S14†), which helps to explain the low methane content in the final products.

Conclusions

In summary, we have developed a strategy for ethanol synthesis from paraformaldehyde, CO_2 and H_2. The reaction can be effectively accelerated by a Ru–Co bimetallic catalyst. Ethanol can be generated at above 140 °C. The TOF of ethanol based on Ru metal can be as high as 17.9 h^{-1} at 180 °C, and the selectivity of ethanol in the total products reaches 50.9 C-mol%. In addition, the catalytic system can be easily reused and the TON of ethanol exceeds 805 after 5 cycles. This route can be applied for paraformaldehydes of different molecular weights. The high efficiency of this process can be ascribed to the good synergy of the cascade reactions. The Ru and Co catalysts also work cooperatively to promote the reaction. This protocol offers a new way for ethanol production and CO_2 utilization.

Experimental

Chemicals

Ruthenium(III) acetylacetonate ($Ru(acac)_3$, 98%), dodecacarbonyl triruthenium ($Ru_3(CO)_{12}$, purity >98%), ruthenium(III) chloride ($RuCl_3$, 99%), dichlorotris(triphenylphosphine) ruthenium(II) ($(PPh_3)_3RuCl_2$, 97%), nickel(II) acetylacetonate ($Ni(acac)_2$, 98%), manganese(III) acetylacetonate ($Mn(acac)_3$, 98%) and lithium bromide (LiBr, 99.5%) were purchased from Adamas Reagent. Paraformaldehyde (97%), cobalt(II) bromide ($CoBr_2$, 99.5%), cobalt(II) iodide (CoI_2, 99.5%), chlorotris(triphenyl phosphine) cobalt(I) ($(PPh_3)_3CoCl$, 97%), lithium iodide (LiI, 99.95%), sodium iodide (NaI, 99.95%), ruthenium(III) bromide hydrate ($RuBr_3$, Ru 25% min), potassium iodide (KI, 99.9%), iridium acetate ($Ir(OAc)_n$, Ir 48–54%), iron nonacarbonyl ($Fe_2(CO)_9$, 99%), hexarhodium hexadecacarbonyl ($Rh_6(CO)_{16}$, 98%) and 1-methyl-2-pyrrolidinone (NMP, 99%) were provided by Alfa Aesar China Co., Ltd. Iron(III) acetylacetonate ($Ir(acac)_3$, 99+%), copper(II) bromide ($CuBr_2$, 99%) and nickel(II) bromide ($NiBr_2$, 99%) were purchased from Acros Organics Company. Lithium chloride (LiCl, 98%) and 1,3-dimethyl-2-imidazolidinone (DMI, 98%) were obtained from TCI Shanghai Co., Ltd. Cobalt(II) chloride ($CoCl_2$, 99%), cobalt(II) acetylacetonate ($Co(acac)_2$, 99%), *N*,*N*-dimethylformamide (DMF, 99.5%), 1,3,5-trioxane (99%), tetrahydrofuran (THF, 99.5%) and cyclohexane (99%) were purchased from J&K Scientific Ltd. Toluene (99.8%) was obtained from Xilong Chemical Co., Ltd. ^{13}C paraformaldehyde (99 atom% ^{13}C) was supplied by Cambridge Isotope Laboratories, Inc. CO_2 (99.99%), H_2 (99.99%) and CO (99.99%) were purchased from Beijing Analytical Instrument Company. All chemicals were used as received.

Catalytic reaction

The apparatus and procedures were similar to that reported previously.[3c,7,9a] All the experiments were carried out in a 16 mL Teflon-lined stainless steel reactor equipped with a magnetic stirrer. The inner diameter of the reactor was 18 mm. In a typical experiment, certain amounts of the Ru and/or Co catalyst, LiI or another promoter, paraformaldehyde or tracer (if used) and 2 mL solvent were added into the reactor. At room temperature, CO_2 and H_2 were charged sequentially into the reactor to the desired pressure after the reactor was purged with 1 MPa CO_2 for three times. The reactor was placed in an air bath at constant temperature, and the magnetic stirrer was set at 800 rpm. After the reaction was complete, the reactor was cooled in an ice-water bath. Then the residual gas was released slowly and collected in a gas bag. Using toluene as the internal standard, the reaction solution was analyzed by GC (Agilent 7890B) equipped with a flame ionization detector and a HP-5 capillary column (0.32 mm in diameter and 30 m in length). The liquid products were identified using GC-MS (Agilent-7890B-5977A) as well as by comparing the retention times with the standards in the GC traces. The yields of the products were calculated from the GC data. NMR data were obtained on a Bruker Avance III HD 400 MHz NMR spectrometer (^1H NMR, 400 MHz; ^{13}C NMR, 100 MHz). The gaseous samples were detected by 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 carrier gas.

Recycling test

After the reaction, the reactor was cooled in an ice-water bath for 2 h and the residual gas was released slowly. The amount of the product was determined by the above method. The products generated in the reaction were removed under vacuum at 85 °C for 5 h, which was affirmed by GC analysis. Then the catalytic system was used directly for the next cycle.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The authors thank the National Natural Science Foundation of China (21373234 and 21533011), the National Key Research and Development Program of China (2017YFA0403102), and the Chinese Academy of Sciences (QYZDY-SSW-SLH013).

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