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Efficient Synthesis of Acetic Acid via Rh Catalyzed Methanol Hydrocarboxylation with CO₂ and H₂ at Milder Condition⁺

Meng Cui,^{a,b} Qingli Qian,^{*a} Jingjing Zhang,^{a,b} Chunjun Chen,^{a,b} and Buxing Han^{*a,b}

Acetic acid is an important bulk chemical and synthesis of acetic acid via methanol hydrocarboxylation with CO₂ and H₂ is a very promising route. In this work, we studied the reaction over a number of catalytic systems. It was found that Rh₂(CO)₄Cl₂ with 4-methylimidazole (4-MI) as the ligand was very efficient in the presence of LiCl and Lil. Acetic acid began to form at 150 °C. The TOF was as high as 26.2 h⁻¹ and the yield of acetic acid could reach 81.8% at 180 °C. The catalytic system had obvious advantages, such as simple, high activity and selectivity, milder reaction condition, and less corrosive. The excellent cooperation of CO and Cl⁻ in the Rh₂(CO)₄Cl₂, suitable basicity and aromaticity of the ligand 4-MI, and the hydrogen bonding ability of Cl⁻ were crucial for the outstanding performance of the catalytic system. The control experiments showed that the reaction did not proceed via со pathway.

Introduction

Carbon dioxide (CO₂) is a highly abundant, renewable, easily available, nontoxic carbon resource.¹ Utilization of CO_2 as C1 synthon has attracted much attention in recent years, and many valuable chemicals and fuel have been synthesized, such as alcohols, hydrocarbons, carboxylic acids, formamides, carbonates, esters, and so on.² Carboxylic acids are important and basic chemicals in industry and human life. Considerable progress has been made in formic acid synthesis using CO₂ and H₂ after intensive research for several decades.³ The carboxylic acids with two or more C atoms (C_{2+}) are more useful in many cases.⁴ However, synthesis of C_{2+} carboxylic acids using CO₂ usually uses expensive and/or particular substrates, such as alkenes, alkynes, arenes, and/or organic halides, and the metallic reducing agents are generally utilized.⁵ Transformation of CO_2 into C_{2+} carboxylic acids using cheap and easily available feedstocks is of great importance, but is challenging. At present stage, the related progress was seldom reported. In a pioneering work, carboxylic acids were synthesized using olefins with CO₂ and H₂, in which several examples of carboxylic acid (other than acetic acid) synthesis using corresponding alcohols with CO₂ and H₂ were discussed.⁶ It was reported that the reactions followed the CO pathway under the reaction condition.

Acetic acid is an important bulk chemical that is currently produced via methanol carbonylation technology using fossil resource based CO.⁷ So far, only several preliminary results of acetic acid synthesis using CO₂ were reported.⁸⁻¹¹ For example, small amount of acetic acid could form via the direct co-conversion of CH₄ and CO₂, for which severe reaction conditions are required because of the unfavorable thermodynamics.⁸ The reduction of CO₂ by iron nanoparticles at 200 °C could generate acetic acid with very low activity (<0.05 mmol \bullet L⁻¹ \bullet h⁻¹) and selectivity (<28.5 mol%).⁹ Trace amount of acetic acid was observed in CO₂ hydrogenation at 200 °C, but the product spectrum was broad and CO accounted for 96% of the total products.¹⁰ When the expensive and toxic methyl iodide reacted with CO_2 and H_2 by homogeneous catalysis at 240 $^{\circ}$ C, minor acetic acid (10.7%) was produced with CO (58.4%) and CH_4 (30.9%). Furthermore, the acetic acid only formed in the presence of two transition metals (Ru/Co or Ni/Co) and the TOF of acetic acid was low $(<1.4 h^{-1})$.¹¹ The progress in this area was very slow in the past. Currently, the CO₂ hydrogenation with simultaneous C-C bond formation is a grand challenge in CO₂ chemistry.¹²

Recently, we reported a route to produce acetic acid via methanol hydrocarboxylation with CO₂ and H₂.¹³ This route is very promising because it utilizes cheap and easily available feedstocks and the efficiency is high. It is a potentially practical way to fix CO₂ into value-added chemical on a large scale, although breakthroughs need to be made before this route is industrially viable. It is obvious that exploration of efficient and simple catalytic systems, decreasing reaction temperature, avoiding or reducing the dosage of corrosive additives are of great importance from both scientific and practical viewpoints.

In this work, we found that monometallic catalytic system consisting of Rh₂(CO)₄Cl₂, 4-methylimidazole (4-MI), LiCl and Lil was very efficient for acetic acid synthesis from CO₂, methanol and H₂ (Scheme 1). The catalytic system have some obvious advantages,

Rh-(4-MI)-LiCI-LiI $CH_3OH + CO_2 + H_2$ CH₃COOH > 150 °C, in DMI

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Scheme 1 Synthesis of acetic acid via methanol hydrocarboxylation with CO₂ and H₂.

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such as simple, high activity and selectivity, lower reaction temperature, and the amount of corrosive Lil used was reduced significantly. Detailed study showed that the cooperation of CO and Cl^- in the $Rh_2(CO)_4Cl_2$, suitable basicity and aromaticity of the ligand 4-MI, and the hydrogen bonding ability of Cl^- were crucial for the outstanding performance of the catalytic system. The reaction mechanism was proposed on the control experiments, which indicated that the reaction did not proceed via CO pathway.

Results and discussion

Different catalytic systems were tested to synthesize acetic acid from CO₂, methanol and H₂, and the results are shown in Table 1. The product in the reaction solution was mostly acetic acid, and other products were negligible (Fig. S1 and Fig. S2). Only a small part of methanol was converted into CH₄. The solvent DMI was stable at reaction condition, and no decomposed product was detected. At 180 °C, the turnover frequency (TOF) and yield of acetic acid could reach 26.2 h⁻¹ and 81.8%, respectively (entry 1), which are much higher than that of the reported Ru-Rh bimetallic catalyst (10.1 h⁻¹ and 23.2%) at the same temperature.¹³ Besides avoiding use of noble Ru compound, the amount of corrosive iodide salt was only 1/3 of that in the reported catalytic system.¹³ In brief, this catalyst is more efficient, less corrosive and could work at milder condition.

Effective cooperation between different components of the catalyst is the key for its outstanding catalytic performance. In the absence of one or more components, the catalyst behaved poorly or did not work (entries 2-5). The Rh catalyst was the basis of the catalytic property and the structure of the Rh precursor played a decisive role. When RhI_3 was used as precursor, trace acetic acid could be detected and evident black precipitate was observed after reaction (entry 6). When RhI₃ was changed to RhBr₃, the catalytic activity had a minor increase but the catalyst was still unstable (entry 7). After the reaction using RhCl₃ as precursor, the generation of acetic acid had an obvious increase. Moreover, the catalyst became stable (entry 8). These indicated that the presence of Cl⁻ in the Rh precursor is beneficial to enhancing the activity and stability of the catalyst. When $Rh_6(CO)_{16}$ was used as precursor, no acetic acid was produced and the catalyst was unstable (entry 9). To our surprise, the carbonyl group (CO), which was invalid for the reaction in $Rh_6(CO)_{16}$, could cooperated very well with the Cl in $Rh_2(CO)_4Cl_2$ and greatly enhanced the catalytic activity (entry 1). The cooperation of CO and Cl in Rh₂(CO)₄Cl₂ was neccessary because no acetic acid was observed when the Rh precursors containing Cl⁻ and another ligand were utilized (entries 10 and 11). Furthermore, when a third ligand was introduced into the Rh precursor including Cl and CO, the catalyst did not work either (entry 12). When we tested $Rh_2(OAc)_4$, the Rh precursor used in the previous work,¹³ only minor acetic acid was formed and the catalyst was unstable (entry 13). Hence the $Rh_2(CO)_4Cl_2$ was a suitable catalyst for the target reaction. The synergy of Cl⁻ and CO in the Rh precursor could affect the nature of the active Rh species formed in situ,¹⁴ which may account for the excellent performance of the $Rh_2(CO)_4Cl_2$ in the reaction. Although the $Rh_2(CO)_4Cl_2$ could catalyze the formation of acetic acid at low content of the corrosive iodide promoter, the catalytic activity was low and the catalyst was not

stable (entry 2). Thus cocatalyst may be needed to immove the property of the catalyst. Inspired by the Prove of Prove the Prove of the catalyst. Inspired by the Prove of Pro

atom, but no acetic acid was produced (entry 16). When some common metallic chlorides (KCI, NaCI) were used as cocatalyst, respectively, the formation of acetic acid was not observed either (entries 17 and 18). Remarkable acetic acid was generated and the catalyst was stable when LiCI was used (entry 1). The superiority of

Table 1 Methanol hydrocarboxylation with CO2 and H2 using different catalytic systems ^a							
Entr /	Catalyst precursors	Ligan d	Cocatal yst	Prom oter	Solve nt	TOF (h ⁻¹) ^b	Yield (%) ^c
1	Rh ₂ (CO) ₄ Cl ₂	4-MI	LiCl	Lil	DMI	26.2	81.8
2 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	-	Lil	DMI	5.5	17.0
3 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	LiCl	-	DMI	0	0
1 ^{<i>d</i>}	Rh ₂ (CO) ₄ Cl ₂	-	LiCl	Lil	DMI	0	0
5 ^d	Rh ₂ (CO) ₄ Cl ₂	-	-	-	DMI	0	0
5 ^d	Rhl₃	4-MI	LiCl	Lil	DMI	0.1	0.5
7 ^d	RhBr₃	4-MI	LiCl	Lil	DMI	0.4	1.1
3	RhCl₃	4-MI	LiCl	Lil	DMI	11.2	34.9
Θ^d	Rh ₆ (CO) ₁₆	4-MI	LiCl	Lil	DMI	0	0
10 ^d	Rh(PPh₃)₃Cl	4-MI	LiCl	Lil	DMI	0	0
11 ^d	[Rh(1,5- COD)Cl] ₂	4-MI	LiCl	Lil	DMI	0	0
12 ^d	RhCl(CO)(PPh 3)2	4-MI	LiCl	Lil	DMI	0	0
13 ^d	Rh ₂ (OAc) ₄	4-MI	LiCl	Lil	DMI	6.8	21.2
14	$Rh_2(CO)_4Cl_2$	4-MI	HCI	Lil	DMI	0	0
15 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	[Hmim] Cl	Lil	DMI	0	0
16 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	TBAC	Lil	DMI	0	0
17 ^d	$Rh_2(CO)_4Cl_2$	4-MI	NaCl	Lil	DMI	0	0
18 ^d	$Rh_2(CO)_4Cl_2$	4-MI	KCI	Lil	DMI	0	0
19 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	LiBr	Lil	DMI	0	0
20 ^d	$Rh_2(CO)_4Cl_2$	4-MI	Lil	Lil	DMI	0.9	2.7
21 ^d	$Rh_2(CO)_4Cl_2$	4-MI	$LiBF_4$	Lil	DMI	9.5	29.8
22 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	Li[2- CBZ]	Lil	DMI	0	0
23 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	LiCl	LiBr	DMI	0	0
24 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	LiCl	LiCl	DMI	0	0
25 ^d	$Rh_2(CO)_4Cl_2$	4-MI	LiCl	Nal	DMI	3.1	9.6
26 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	LiCl	KI	DMI	2.4	7.3
27	$Rh_2(CO)_4Cl_2$	4-MI	LiCl	Lil	NMP	3.2	10.1
28 ^d	$Rh_2(CO)_4Cl_2$	4-MI	LiCl	Lil	DMF 1,4-	0	0
29 ^d	$Rh_2(CO)_4Cl_2$	4-MI	LiCl	Lil	Dioxa ne	0	0
30 ^d	Rh ₂ (CO) ₄ Cl ₂	4-MI	LiCl	Lil	H ₂ O	0	0

^aReaction conditions: 30 µmol Rh catalyst (based on the metal), 0.5 mmol 4-MI, 4 mmol cocatalyst, 1 mmol promoter, 2 mL solvent, 12 mmol methanol, 5 MPa CO_2 and 5 MPa H_2 (at room temperature), 180 °C, 15 h. ^bTOF denotes moles of acetic acid produced per mole of Rh catalyst per hour in the steady state. ^cYield is based on methanol feedstock (100 × moles of acetic acid product per mole of methanol feedstock). ^dBlack precipitate was observed after the reaction.

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LiCl may lie in its good solubility in the reaction solvent, the stronger Lewis acidity, and proper ion size of the Li⁺. We also conducted experiments with other lithium salts (LiBr, Lil, LiBF₄), but the catalytic results were poor (entries 19-21). It seemed that the combination of Li and Cl could give the best results. We further tested lithium 2-chlorobenzoate (Li[2-CBZ]), but no acetic acid was found after reaction (entry 22). This indicates that LiCl is the best cocatalyst for the selected Rh catalyst. Although the usage of the corrosive Lil promoter has been greatly decreased in this work, it is still indispensable for the reaction (entry 3). When other lithium halides (LiBr, LiCl) were used as promoter, no acetic acid could be detected either (entries 23 and 24). We also tried other alkali metal iodides (NaI, KI), but the catalytic performance was unsatisfactory (entries 25 and 26). Thus Lil was the best promoter for the catalyst. The superiority of Li⁺ may be ascribed to its stronger Lewis acidity and proper size, which would render better coordination sites in the reaction. The better performance of I may be due to its peculiar nature.¹⁵ Firstly, the "soft" iodide ligand binds more firmly to soft metals (such as Rh) than the other halides or ligands, which is beneficial to the catalyst stability. Secondly, the size of I is larger than other halides and may block nucleophilic attack to Rh, offering better catalytic selectivity. Thirdly, I may also participate in different steps of transition metal catalyzed reaction, such as oxidative addition, reductive elimination, and substrate activation. These properties may facilitate the formation of C-C bond in acetic acid formation. After screening the solvents, we found that 1,3dimethyl-2-imidazolidinone (DMI) was the best for the reaction (entries 27-30). As a weak Lewis base, DMI may not only help to stabilize the catalyst, but also help to absorb and activate the acidic CO₂.

The ligand is also crucial to the catalytic performance and it played a distinctive role in this work. Without ligand, the Rh monometallic catalyst could not catalyze the target reaction and it was unstable (entry 4 of Table 1). To get further understanding of the ligand effects, we conducted systematic research, and the results are given in Table 2. Firstly, we tested the commonly used PPh₃, but no acetic acid was generated and the catalyst was unstable (entry 1). Then we tried NEt₃, but acetic acid could not form either (entry 2). In addition, the catalyst was not stable. When we turned to use pyridine, the catalyst was stable and minor acetic acid was observed after reaction (entry 3). We further tried pyrrole, a heterocyclic monoamine containing N atom of different nature, but the catalyst had no activity and was unstable (entry 4). The reason may be that the Lewis basicity of pyridine is stronger than that of pyrrole, rendering better coordination capability with the Rh catalyst. We further studied the performance of piperidine, which has the same C/N skeleton with pyridine and much stronger basicity, but it was not effective for the reaction (entry 5). Thus both basicity and aromaticity of the ligand are important for the performance of the catalyst.

We also studied the effect of 2,2'-bipyridine and pyrimidine, which has two pyridinic N atoms, but the results were poor (entries 6 and 7). When O or S atom coexisted with pyridinic N atom in a heterocyclic ring, the catalytic performance had little improvement (entry 8) or was totally inhibited (entry 9). However, when imidazole was utilized in the reaction, the catalyst had much better activity, selectivity and stability (entry 10). It is well known that

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imidazole has two kinds of N atoms, namely, the pyridinic N atom and the pyrrolic N atom.¹⁶ The X-ray photoelectron spectroscopy (XPS) study revealed that the pyridinic N atom coordinated with the Rh catalyst (Fig. S3). The lone pair electrons of the pyrrolic N atom participates in forming conjugated π bond of the heterocycle and enhances the coordination capability of the pyridinic N atom, which can explain the better performance of the imidazole as the ligand. When pyrazole, an isomer of imidazole with much lower coordination ability, was used as ligand, the catalytic performance

Table 2 Effect of d	Table 2 Effect of different ligands on methanol hydrocarboxylation with CO_2 and H_2^{-1}					
Entry	Ligand	TOF (h ⁻¹)	Yield (%)			
1 ^{<i>b</i>}	0,0	0	0			
2 ^{<i>b</i>}	N	0	0			
3		6.2	19.2			
4 ^{<i>b</i>}	< No.	0	0			
5 ^{<i>b</i>}	() H	0	0			
6		0	0			
7		3.3	10.2			
8	<pre>N</pre>	9.4	29.3			
9 ^b	∠_s	0	0			
10		21.9	68.3			
11	< N N	3.0	9.5			
12	N N	10.1	31.5			
13	N N N N N N N N N N N N N N N N N N N	6.2	19.3			
14		15.4	47.9			
15	CI N	3.4	10.6			
16 ^{<i>b</i>}	HOOC	0	0			
17	Z NH	26.2	81.8			
18	Z Z Z	18.4	57.5			
19	∑ _N ×	18.2	56.7			
20	ZT.	17.1	53.4			
21 ^b	<pre>K</pre>	5.7	17.9			
22 ^b	K SHI	7.0	27.9			
23		9.6	29.9			

^aReaction conditions: 30 μmol Rh₂(CO)₄Cl₂ (based on the metal), 0.5 mmol ligand, 4 mmol LiCl, 1 mmol Lil, 2 mL DMI, 12 mmol methanol, 5 MPa CO₂ and 5 MPa H₂ (at room temperature), 180 °C, 15 h. ^bBlack precipitate was observed after the reaction.

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was poor (entry 11). We also tested triazole and tetrazole, respectively, which have similar structures with imidazole but lower coordination capacity, the results were not satisfactory (entries 12 and 13). The H atom linked to the pyrrolic N atom also played an important role. When it was replaced by a methyl group, the catalytic performance became poorer evidently (entry 14). One of the possible reasons may be that the N-H formed hydrogen bond with Cl⁻, improving the electronic effect of the ligand.^{16,17} The Cl⁻ is much easier to form hydrogen bond with N-H than Br⁻ or l⁻, which would explain the superiority of LiCl and/or chloric Rh precursor in the reaction.

The substituent groups on the C atoms of the imidazole also markedly affected the catalytic performance. As a whole, the electron withdrawing group, such as -Cl and -COOH, greatly inhibited the reaction (entries 15 and 16). Because of conjugative effect, the decrease of electron density on the heterocycle weakens the coordination capability of the pyridinic N atom, thus hampering the catalytic performance. As for the electron donating group, such as alkyl groups or -SH, the electronic effect should be beneficial to the catalytic properties. The actual influence of such substituents depended on the balance between the electronic and steric effects. For example, when we used 4-MI, the electronic effect dominated and the catalytic performance was improved significantly (entry 17). However, if the electron donating substituents located next to the pyrrolic N, the steric effects dominated and the catalytic activity decreased evidently (entries 18-22). There is a strong possibility that particular synergy existed between the two N atoms of imidazole during the catalytic reaction. The substituents next to the pyrrolic N would hinder the synergy, destroying the catalytic properties. The ligand with more complicated substituent was also tested, but the catalytic performance was unsatisfactory (entry 23). In short, the 4-MI could effectively improve the stability and activity of the Rh catalyst.

The impact of gas pressure and catalyst dosage on the reaction were studied, and the results are presented in Table 3. At the fixed ratio of CO_2 and H_2 (1:1), the yield of acetic acid increased evidently when the total pressure was increased

Table 3 Effect of reaction parameters on methanol hydrocarboxylation with CO₂ and

H_2^{a}		•	,			
Entry	Rh (μmol)	pCO₂ (MPa)	pH₂ (MPa)	TOF (h⁻¹)	Yield (%)	
1	30	2	2	0	0	
2	30	3	3	1.3	4.2	
3	30	4	4	15.8	49.3	
4	30	5	5	26.2	81.8	
5	30	6	6	27.8	86.7	
6	30	2	8	4.5	14.2	
7	30	4	6	17.1	53.5	
8	30	6	4	18.6	57.9	
9	30	8	2	1.9	5.8	
10^{b}	30	5	0	0	0	
11^{b}	30	0	5	0	0	
12	20	5	5	12.9	40.2	
13	40	5	5	26.8	83.7	

^{*a*}Reaction conditions: Rh₂(CO)₄Cl₂ was used as catalyst precursor and its dosage was based on the metal, 0.5 mmol 4-MI, 4 mmol LiCl, 1 mmol Lil, 2 mL DMI, 12 mmol methanol, 180 ^{*a*}C, 15 h. ^{*b*}Black precipitate was observed after the reaction.

from 4 MPa to 10 MPa (entries 1-4). But the improvement of the catalytic performance became mindr¹⁰ when the ⁰¹ total pressure was further raised (entries 4 and 5). When the total pressure was fixed at 10 MPa, the results showed that the ratio of CO₂ and H₂ affected the efficiency of the catalytic system, and the best result occurred at 5 MPa CO₂ and 5 MPa H₂ (entries 4, and 6-9). The reaction did not occur without CO₂ or H₂ (entries 10 and 11). Hence both CO₂ and H₂ were necessary for acetic acid generation and 5 MPa CO₂/5 MPa H₂ was suitable for the target reaction. The catalytic efficiency was enhanced with the elevation of the catalyst dosage, but it was less sensitive when the dosage was large enough (entries 4, 12 and 13).

The dosage of 4-MI, LiCl and Lil also remarkably influenced the catalytic performance (Figs. 1a-1c). With the increase of these components, the yield of acetic acid increased quickly. However, excess amount of them could suppress the catalytic performance. Just like 4-MI, the Cl⁻ and l⁻ may also act as ligand, and too much of them would occupy the active sites of the catalyst, inhibiting the reaction. The optimal usage of 4-MI, LiCl and Lil was 0.5 mmol, 4 mmol and 1 mmol, respectively. Fig. 1d illustrates the effect of reaction temperature. Acetic acid began to form at 150 °C, and the yield increased rapidly with the elevating temperature until 180 °C. When the temperature was further enhanced, the change of catalytic activity became slow. Thus the appropriate reaction temperature was 180 °C. Fig. 1e depicts the time course of the reaction. At the beginning (0-3 h), methyl acetate appeared and increased because the esterification between methanol and acetic acid generated in situ. After 3 h, obvious molecular acetic acid was



Fig. 1 Effect of reaction conditions (a-f) over 30 µmol Rh₂(CO)₄Cl₂ (based on the metal) in 2 mL DMI with 12 mmol methanol at 5 MPa CO₂ and 5 MPa H₂: (a) Effect of 4-MI dosage, 4 mmol LiCl, 1 mmol Li1, 180 °C, 15 h; (b) Effect of LiCl dosage, 0.5 mmol 4-MI, 1 mmol Li1, 180 °C, 15 h; (c) Effect of Lil dosage, 0.5 mmol 4-MI, 4 mmol LiCl, 180 °C, 15 h; (d) Effect of reaction temperature, 0.5 mmol 4-MI, 4 mmol LiCl, 1 mmol LiI, 15 h; (e) and (f) Effect of reaction time, 0.5 mmol 4-MI, 4 mmol LiCl, 1 mmol LiI, 180 °C.

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detected and it grew continuously with reaction time (3-15 h). The reaction slowed down when methanol was gradually used up (15-18 h). As expected, the methyl acetate generated initially was transformed into acetic acid due to the reverse esterification. Because hydrogenation of acetic acid into ethanol at the reaction condition is very difficult, only trace ethanol and/or ethyl acetate were detected after the reaction. The consumption of CO₂ was consistent with the formation of acetic acid, and no CO was detected during the reaction (Fig. 1f). We also studied the recyclability of the catalytic system, and the catalytic activity did not decrease obviously after three cycles (Fig. S4). These phenomena suggest that the Rh monometallic catalyst could effectively promote the methanol hydrocarboxylation with CO₂ and H₂ into acetic acid.

To understand the mechanism of the reaction, we conducted the experiment using CO to replace CO₂, and other conditions were the same as that given in entry 1 of Table 1, no acetic acid was formed (Fig. S5), demonstrating that reaction did not proceed via CO route. We also tried a control experiment without methanol, both acetic acid and CO were not detected (Fig. S6). Therefore, this work is different from the well known Rh catalyzed methanol carbonylation with CO. To get further evidence for this argument, we conducted tracer experiments using ¹³CH₃OH, CH₃¹⁸OH and CH₃OD, respectively (Figs. S7-S10). When ¹³CH₃OH was used, the molecular weight of acetic acid formed in the reaction was 61 Daltons (Fig. S7), indicating that the two C atoms in the acetic acid product were from ^{13}C of $^{13}\text{CH}_3\text{OH}$ and C of CO_2, respectively. When CH₃¹⁸OH was used to replace methanol, the molecular weight of acetic acid was still 60 Daltons (Fig. S8), demonstrating that both O atoms in the product were from CO₂, and the OH group in the methanol was removed in the reaction. Moreover, as methanol was replaced by CH₃OD in the reaction, the molecular weight of acetic acid generated in the reaction was also 60 Daltons (Fig. S9), further indicating that both O atoms in the product were from CO₂, and the OH group in the methanol was removed in the reaction. In addition, ¹H NMR and ¹³C NMR study showed that CH₃ group of CH₃OH was transferred into the acetic acid product in the reaction (Fig. S10). All the results supported the conclusion that CO₂ took part in the reaction directly, and the reaction did not follow CO pathway.



Scheme 2 Proposed mechanism of the reaction over the Rh-based catalytic system.

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On the basis of the experimental results, we proposed the possible reaction mechanism as shown PPSdReARe/27 WRIGHIS similar to that of the reported catalyst.¹³ Firstly, methyl iodide (CH₃I) was generated spontaneously from methanol and LiI (Step 1). The second step was the oxidative addition of CH₃I to the Rh active species (Rh*) (Step 2). Thirdly, CO₂ inserted into CH₃Rh*I to form CH₃COORh*I (Step 3). Next step was reductive elimination of acetic acid from the CH₃COORh*I with the participation of H₂ (Step 4). Finally, the LiOH reacted spontaneously with HI to form Lil and H₂O (Step 5). At this time, all the catalytic species were regenerated for the next cycle. The 4-MI, with particular structure and strong coordination capability, was beneficial to the oxidative addition of CH₃I (Step 2) and insertion of CO_2 (Step 3),^{7, 18} which are two basic and key steps of the reaction. With close cooperation with the 4-MI, LiCl and Lil, the Rh monometallic catalyst not only promoted all the catalytic steps smoothly, but also effectively lowered the reaction temperature.

Conclusions

In summary, we have investigated the performance of Rhbased monometallic catalysts for methanol hydrocarboxylation with CO₂ and H₂ to produce acetic acid. It is demonstrated that the catalytic system consisting of Rh₂(CO)₄Cl₂, 4-MI, LiCl, and Lil has excellent activity and selectivity for the reaction at milder condition. At 180 °C, the TOF and yield of acetic acid can reach 26.2 h^{-1} and 81.8%, respectively. In the reaction, CO₂ is inserted into the intermediate directly, and the reaction does not proceed via CO pathway. The catalyst components cooperate very well in accelerating the target reaction. The Rh₂(CO)₄Cl₂, 4-MI, and Lil contribute to the formation of acetic acid, and LiCl greatly promotes the catalytic activity and stabilizes the catalyst. In addition, Rh₂(CO)₄Cl₂ is unique in that CO and Cl⁻ cooperatively promote the reaction. Ligand 4-MI is a very efficient ligand because it has suitable basicity and aromaticity. This process is greener because it uses CO₂ as feedstock, and in comparison with Ru-Rh bimetallic catalyst, the catalytic system is simpler, less corrosive and more efficient at milder condition.

Experimental

Chemicals

Tetracarbonyl di-µ-chlorodirhodium(I) (Rh₂(CO)₄Cl₂, 97%) was purchased from Acros Organics. Rhodium acetate dimer (Rh₂(OAc)₄), lithium chloride (LiCl, 98%), and 1,3-dimethyl-2imidazolidinone (DMI, 98%) were provided by TCI Shanghai Co., Ltd. Hexarhodium hexadecacarbonyl (Rh₆(CO)₁₆, 98%), rhodium(III) chloride (RhCl₃, Rh > 38.5%), rhodium(III) bromide (RhBr₃), rhodium(III) iodide (Rhl₃, 99.9%), carbonylchlorobis(triphenylphosphine)rhodium(I)(RhCl(CO)(PP h₃)₂, Rh 14.9% min), lithium iodide (Lil, 99.95%), lithium bromide (LiBr, 99%), lithium tetrafluoroborate (LiBF₄, 98%), lithium hydroxide monohydrate (LiOH, 56.5%), sodium iodide (Nal, 99.5%), sodium chloride (NaCl, 99.99%), potassium iodide

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(KI, 99.9%), potassium chloride (KCl, 99.99%), imidazole (99%), 2-methylimidazole (97%), 2,4-dimethylimidazole (97%), 2mercaptoimidazole (98%), 4,5-dichloroimidazole (98%). benzimidazole (99%), pyridine (99%), triphenylphosphine (PPh₃, 99%), triethylamine (99%), piperidine (98%), 2,2'-bipyridine (99%), and 1-methyl-2-pyrrolidinone (NMP, 99%) were obtained from Alfa Aesar China Co, Ltd. 4,5-Dimethylimidazole (95%) was obtained from Accela ChemBio Co., Ltd. Tetrabutylammonium chloride (TBAC, 98%), chlorotris(triphenylphosphine)rhodium(I) (Rh(PPh₃)₃Cl, 98%), chloro(1,5-cyclooctadiene) rhodium(I) dimer ([Rh(1,5-COD)Cl]₂, 98%), pyrrole (99%), 1,2,4-triazole (99%), and methanol-D1 (CH₃OD, 99.5 atom% D) were purchased from Beijing InnoChem Science & Technology Co., Ltd. Pyrazole (99%), pyrimidine (98%), thiazole (99%), 1-methylimidazole (99%), 4methylimidazole (4-MI, 98%), and 2-chlorobenzoic acid (98%) were provided by J&K Scientific Ltd. Tetrazole (98%), 2propylimidazole (98%), imidazole-4-carboxylic acid (98%), and oxazole (97%) were obtained from Adamas Reagent Co., Ltd. 1-Hexyl-3-methylimidazolium chloride ([Hmim]Cl, purity > 99%) was purchased from the Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Hydrochloric acid (HCl, 37% solution in water), N,N-dimethylformamide (DMF, 99%), 1,4-dioxane (99%), and methanol (99.5%) were purchased from Beijing Chemical Company. Toluene (99.8%) was obtained from Xilong Chemical Co., Ltd. Methanol-¹³C (¹³CH₃OH, 99 atom% ¹³C) and methanol-¹⁸O (CH₃¹⁸OH, 95 atom% ¹⁸O) were provided by Sigma-Aldrich Co. LLC. CO_2 (99.99%) and H_2 (99.99%) were supplied by Beijing Analytical Instrument Company. All chemicals were used as received.

Preparation of lithium 2-chlorobenzoate (Li[2-CBZ])

The preparation follows a typical acid-base neutralization procedure. To prepare Li[2-CBZ], 20 mmol LiOH·H₂O was dissolved in 30 mL water, 20 mmol 2-chlorobenzoic acid was dissolved in 20 mL methanol, the above solutions were mixed under stirring. After mechanically stirred for 4 hrs at 80 °C, the solvent was removed using rotary evaporator, and the precipitate named Li[2-CBZ] was obtained. The precipitate was washed with ethanol for 3 times, then, dried in vacuum at 50 °C for 12 hrs.

Catalytic Reaction

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The reactions were carried out in a 16 mL Teflon-lined stainless steel reactor equipped with a magnetic stirrer. In a typical experiment, the desired amount of Rh catalyst, cocatalyst, promoter, ligand, methanol (methanol-¹³C, methanol-¹⁸O or methanol-D1 if used) and 2 mL solvent were added into the reactor. After the air in the reactor was replaced by CO_2 , CO_2 and H₂ were charged into the reactor to the desired pressure at room temperature, respectively. The reactor was placed in an air bath of constant temperature, and the stirrer was started at 800 rpm. After reaction, the reactor was cooled in an ice-water bath and the residual gas was released carefully in a gasbag. The liquid mixture was analyzed by a gas

chromatograph (GC, Agilent 7890B) equipped with racifiame ionization detector (FID) and an HP-5 capillary column using toluene as the internal standard. Identification of the liquid products was done using GC-MS (SHIMADZU-QP2010) as well as by comparing the retention times with respective standards in the GC traces. NMR spectra were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer (¹H NMR, 400 MHz; ¹³C NMR, 100 MHz). The gas mixture were analyzed using a GC (Agilent 4890D) equipped with a TCD detector and a packed column (Carbon molecular sieve TDX-01) using argon as the carry gas.

To test the reusability of the catalytic system, the acetic acid formed in the reaction and the unreacted methanol were removed under vacuum at 85 $^{\circ}$ C for 5 hrs, and then the catalytic system was reused directly for the next run.

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$$CH_{3}OH + CO_{2} + H_{2} \xrightarrow{Rh-(4-MI)-LiCI-LiI} CH_{3}COOH$$

Acetic acid can be efficiently synthesized via methanol hydrocarboxylation with CO_2 and H_2 using Rh monometallic catalyst at milder condition.