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High-performance RuCl₃ Catalyst Systems for Hydro-esterification of Methyl Formate and Ethylene

Yan-Ru Li,^{a,b,c,d} Zhong-Ning Xu,^a Bing Bai,^a Zhi-Qiao Wang,^{a,*} Guo-Cong Guo^{a,*}

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002,

P. R. China.

University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

^b School of Physical Science and Technology, Shanghai Tech University, Shanghai 201210, P. R. China.

^d Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China.

E-mail: gcguo@fjirsm.ac.cn, wangzq@fjirsm.ac.cn; Fax: +86 591 63173068; Tel: +86 591 63173336

RuCl₃ catalyst system has many advantages for the hydro-esterification of methyl formate and ethylene to methyl propionate. However, the unsatisfied performance restricts the development of this route. In this work, high-performance RuCl₃ catalyst systems (RuCl₃-[PPN]Cl-Et₄NI and RuCl₃-NaI) are first reported for this reaction. In RuCl₃-[PPN]Cl-Et₄NI catalyst system, the conversion of methyl formate and the selectivity to methyl propionate are 93.9% and 90.9%, respectively, at mild reaction conditions (165 °C, 2.5 MPa). Noticeably, a simple inorganic RuCl₃-NaI catalyst system achieves 88.8% conversion of methyl formate and 97.6% selectivity to methyl propionate (86.7% yield) at same conditions. NaI, as a promoter, may inhibit the decomposition of methyl formate and be conducive to the formation of methyl propionate. The effects of solvents and promoters are investigated in detail. In addition, the reaction mechanism has been also analyzed. It is hoped to lay a certain foundation for further industrial application.

Introduction

Methyl propionate (MP, CH₃CH₂COOCH₃) is an important chemical material in industry, which is widely used to synthesize perfumes, pharmaceuticals, materials and so on. Significantly, MP also reacts with formaldehyde to synthesize methyl methacrylate (MMA).^[1-5] Because the traditional method (esterification of propionic acid and methanol) is carried out by strong acid catalyst, which leads to equipment corrosion and environmental pollution.^[6-7] In addition, oxidative esterification of propionaldehyde and n-propyl alcohol are using more expensive raw materials and not very high atom economy. Transition metal-catalyzed carbon-hydrogen (C-H) bond functionalization is one of the simplest, most high-effective and environment-friendly to construct carbon-carbon and carbon-heteroatom bonds.^[8-13] So, we choose the hydro-esterification of methyl formate (MF, HCOOCH₃) and ethylene to produce MP.^[14-26]

Thus far, catalysts of the hydro-esterification of MF and ethylene mainly include Palladium compounds, Rhodium compounds and Ruthenium compounds such as Pd(PPh₃)₄, PdCl₂(PPh₃)₂, Rh(CO)Cl(PPh₃)₂, RuCl₂(PPh₃)₂, [PPN][Ru₃(μ-Cl)(CO)₁₀], RuH₂(PPh₃)₂ and so on. Among them, Ruthenium compounds exhibit good catalytic potential.^{[15-16],[24-26]} However, the complicated structure and the high cost of Ruthenium compounds are the main bottlenecks to further apply in industry. So, it is still necessary to develop a stable, simple structure and high performance catalyst system for synthesizing MP from MF with ethylene.

It is a good way to use RuCl₃ to replace expensive, unstable and poisonous Ruthenium compounds as main catalyst and to reduce complex organic ligands and promoters. However, adopting RuCl₃ as main catalyst has not achieved good

performance up to now. For example, Petit et al. got MP yield of 23.5% using RuCl₃-Et₄NI (Et₄NI: Tetraethylammonium Iodide, the molecular structure shown in Fig. S5) as catalyst in DMF solution. However, the reaction required high temperature and high pressure (190 °C, 6 MPa).^[25] Subsequently, Noël Lugan and Guy Lavigne also reported RuCl₃-Et₄NI as catalyst, which only had 11.5% yield at 160 °C and 2 MPa.^[26] It seems difficult to obtain good yield using RuCl₃ as main catalyst in mild condition. In this work, high-performance RuCl₃-[PPN]Cl-Et₄NI catalyst system ([PPN]Cl: Bis(triphenylphosphine)iminium chloride, the molecular structure shown in Fig. S5) is developed for the hydro-esterification of MF and ethylene in DMF as reactive solvent. The 85.4% yield of MP is achieved at a mild reaction condition (165 °C, 2.5 MPa). Then, through explored promoter effects, it is found that NaI is a better promoter to replace [PPN]Cl and Et₄NI and RuCl₃-NaI catalyst system obtains 86.7% yield of MP in this reaction. Finally, the mechanism has been reasonably proposed based on experimental results. This new catalyst system RuCl₃-NaI is benefit for separation and purification from production.

Results and Discussion

The RuCl₃-[PPN]Cl-Et₄NI catalyst system

In the early stages of the study, promoters of [PPN]Cl and Et₄NI were used in the RuCl₃ catalyst system. Through a series of experiments, the optimal reaction condition is at 165 °C for 5 h (Fig. S1). The conversion of MF and the selectivity to MP are 93.9% and 90.9%, respectively, in the mild reaction conditions (165 °C, 2.5 MPa). The pure MP is obtained by vacuum distillation of products. The ¹H NMR spectra of MP is shown in Fig. S11.

1) Exploration the active component and synergistic effect

In order to investigate the active component of the reaction, a

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series of comparative trials were designed, and the corresponding results had been shown in Table 1. In the entry 4, the reaction of synthesizing MP from MF and ethylene happened without the RuCl₃ and promoters ([PPN]Cl and Et₄NI). The conversion of MF is only 2.89%, and the selectivity to MP is 6.02%. When adding [PPN]Cl in the reaction system, the conversion of MF reaches to 14.5%. However, the selectivity to MP is low to 0.97%. When introducing Et₄NI in the reaction system, the conversion of MF is 17.3%. And the selectivity to MP is just 0.69%. Compared with the entry 4, promoters ([PPN]Cl and Et₄NI) improve the conversion of MF, but decrease the selectivity to MP. Interestingly, when only RuCl₃ is added in the reaction system, the conversion of MF reaches to 50.9%, and the selectivity to MP increases to 38.2%. Therefore, the RuCl₃ is the main active component, and the promoters cannot play positive roles in this reaction without RuCl₃.

In order to improve the performance, different promoters were added with main catalyst RuCl₃ to catalyze hydro-esterification of MF and ethylene (Table 2). When introducing [PPN]Cl (entry 6), the conversion of MF is 51.7%, and the selectivity to MP is 51.2%. When adding Et₄NI (entry 7), the conversion of MF is 90.8%, and the selectivity to MP is 75.9%. Compared with entry 1, whether adding [PPN]Cl or Et₄NI in RuCl₃ catalyst system, yields of MP both increases. Specifically, the conversion does not significantly increase, but the selectivity increases obviously under the promotion of [PPN]Cl. While under the promotion of Et₄NI, both the conversion and selectivity increase obviously. When only introducing two promoters (entry 8) without main catalyst RuCl₃, the conversion of MF is 19.1%, and the selectivity to MP is just 0.48%, which means the promoters cannot work by themselves. When main catalyst RuCl₃ and two promoters are all introduced into DMF solvent (entry 5), the conversion of MF and the selectivity to MP reach up to 93.9% and 90.9%, respectively, implying that the RuCl₃-[PPN]Cl-Et₄NI catalyst system works synergistically to achieve the high-performance. Based on IR spectra of promoters and RuCl₃ in DMF, there is no obvious peak shift and new peak in IR spectra suggesting that there is no obvious interaction between promoters and RuCl₃ (Fig. S6 and Fig. S7).

Table 1. Exploration the active component of the reaction.

entry	Catalyst	Promoter1	Promoter2	Conversion (%)	Selectivity (%)	Yield (%)
1	RuCl ₃	-	-	50.9	38.2	19.4
2	-	[PPN]Cl	-	14.5	0.97	14.1
3	-	-	Et ₄ NI	17.3	0.69	11.9
4	-	-	-	2.89	6.02	0.17

Experimental conditions: 16.3 mmol MF, 2.5 MPa ethylene, 0.019 mmol RuCl₃, 0.008 mmol [PPN]Cl, 0.032 mmol Et₄NI, 8 mL DMF, reaction temperature = 165 °C, reaction time = 5 h.

Table 2. Exploration the synergistic effect of the reaction.

entry	Catalyst	Promoter1	Promoter2	Conversion (%)	Selectivity (%)	Yield (%)
6	RuCl ₃	[PPN]Cl	-	51.7	51.2	26.5
7	RuCl ₃	-	Et ₄ NI	90.8	75.9	68.9
8	-	[PPN]Cl	Et ₄ NI	19.1	0.48	9.22
5	RuCl ₃	[PPN]Cl	Et ₄ NI	93.9	90.9	85.4

Experimental conditions: 16.3 mmol MF and 2.5 MPa ethylene, 0.019 mmol RuCl₃, 0.008 mmol [PPN]Cl, 0.032 mmol Et₄NI, 8 mL DMF, reaction temperature = 165 °C, reaction time = 5 h.

Table 3. Exploration the effect of different solvents.

entry	Solution	Conversion (%)	Selectivity (%)	Yield (%)
5	DMF	93.9	90.9	85.4
9	DMA	74.8	64.1	47.9
10	DEF	74.6	57.9	43.2
11	NMF	51.4	8.26	4.24
12	formamide	47.4	0	0
13	methylbenzene	34.8	0	0
14	2-pyrrolidinone	76.6	0	0
15	morpholine	100	0	0
16	n-Butanol	88.9	0	0

Experimental conditions: 16.3 mmol MF and 2.5 MPa ethylene, 0.019 mmol RuCl₃, 0.008 mmol [PPN]Cl, 0.032 mmol Et₄NI, reaction temperature = 165 °C, reaction time = 5 h.

2) Exploration effect of solvents

For entry 4 in Table 1, MP is produced without the RuCl₃ and promoters ([PPN]Cl and Et₄NI), which makes the solvent effect is studied in this catalyst system. As presented in Table 3, DMF is the most suitable solvent, in which the conversion of MF is 93.9%, and the selectivity to MP is 90.9%. In order to investigate the effects of solvents, different organic solvents are adopted with same catalyst system in the optimum condition. The chemical formulas of these solvent molecules are presented in Fig. 1.

On the one hand, considering the α -H atom of DMF (Fig. 1a) replaced by -CH₃ group, the N,N-Dimethylacetamide (DMA, Fig. 1b) as the reaction solvent is chosen, in which the conversion of MF and the selectivity to MP are 74.8% and 64.1%, respectively. On the other hand, when the chemical environment of N atom of DMF is considered, firstly, two -CH₃ groups in DMF are both replaced by -C₂H₅ group. The N,N-Diethylformamide (DEF, Fig. 1c) as reaction solvent is adopted, and the conversion of MF and the selectivity to MP are 74.6% and 57.9%, respectively. Then, the one -CH₃ group of DMF is replaced by H atom. N-Methylformamide (NMF, Fig. 1d) is used, the conversion of MF and the selectivity to MP drop to 51.4% and 8.26%, respectively. When using formamide (Fig. 1e, the two -CH₃ groups in DMF are both replaced by H atom), there is no product of MP. In addition, when using other solvents such as methylbenzene, 2-pyrrolidinone, morpholine and n-Butanol (Fig. 1), they are no catalytic activity for this reaction. So, what is the role of DMF in this reaction?

For studying the role of DMF in this reaction, a series of IR spectra were measured. Samples of a, b, c and d were prepared (in part 5.1 of SI). First, based on literatures, the bending vibration peak of -OCN- group in DMF is at 659 cm⁻¹. And a characteristic

absorption band at 1630–1690 cm^{-1} belong to $\nu_{\text{C=O}}$ of amide group in DMF.^[27–28] In order to analyze the spectra clearly, IR spectra of the bending vibration peak of -OCN- group and amide absorption band of $\nu_{\text{C=O}}$ were presented in Fig. 3 and Fig. 4, respectively. Compared IR spectra of samples a, b, c and d in Fig. 3 and Fig. 4, with the reaction time increasing, the bending vibration peak of -OCN- group (at 659 cm^{-1}) has a blue shift and the characteristic absorption band of $\nu_{\text{C=O}}$ of amide group has a red shift at 1630–1690 cm^{-1} . It means that the energy bound of C=O in DMF may become weak with the reaction time increasing.

According to the report of Francesco Pinna et al., the Ru–O bond is in the range of 992–931 cm^{-1} .^[30] In addition, when DMF is coordinated to Ru, it is O atom of C=O coordinated to Ru.^[24,29] In order to study whether Ru coordinates with DMF in our reaction system, solid samples a and b were prepared (in part 5.2 of SI) and detected them by IR. In Fig. 5, compared the IR spectra of samples a and b, a new peak at 950.9 cm^{-1} should belong to the Ru–O band. Based on above discussions, RuCl_3 is coordinated with DMF in this catalyst system.

Furthermore, Ru XPS spectra of the RuCl_3 -DMF sample and RuCl_3 were measured (Fig. 6). Since the peak of Ru 3d_{3/2} (285.4 eV) overlaps with C 1s (284.8 eV), we analyzed it with a series of 3p peaks. The binding energy (BE) peaks of Ru 3p_{3/2} and 3p_{1/2} in RuCl_3 are 465.2 eV and 487.2 eV, respectively. However, the BE peaks of Ru 3p_{3/2} and 3p_{1/2} in RuCl_3 -DMF sample are 463.6 eV and 485.6 eV, respectively. It is found that the bonding energy of RuCl_3 -DMF sample shifts to low energy (1.6 eV), suggesting that the Ru electron density is increased by DMF. Consequently we propose that RuCl_3 is coordinated with DMF to form intermediate A (RuL) in this system in Fig. 2. Firstly, the lone pair electrons of the nitrogen atom are fed back to the carbon atom causing the C=O bond to break. Then, electron-rich oxygen atom attacks Ru leading to Cl leaved and forming intermediate A. It is important for oxidative addition of MF to form Ru–H active species.^[25,31] Thereby, the structures of solvents play an irreplaceable role in the reaction system.

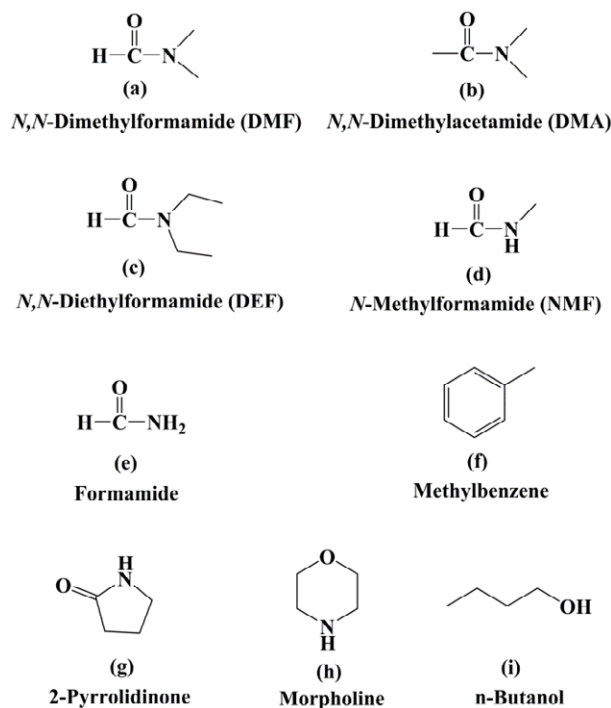


Fig. 1. The chemical formulas of different solvent molecules.

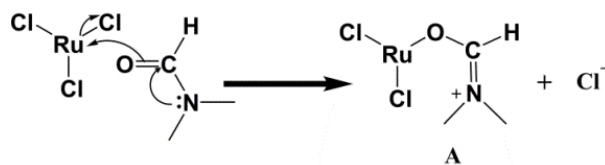


Fig. 2. Schematic diagram of coordination mode of RuCl_3 and DMF.

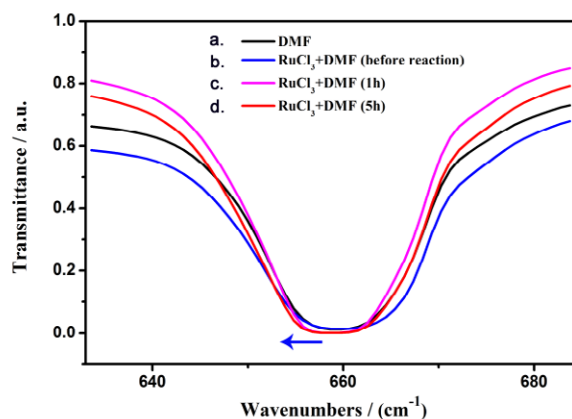
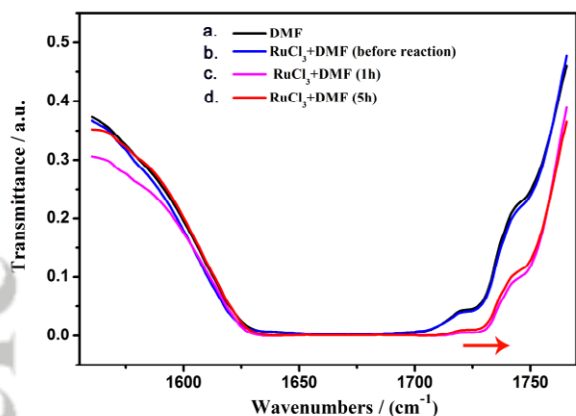
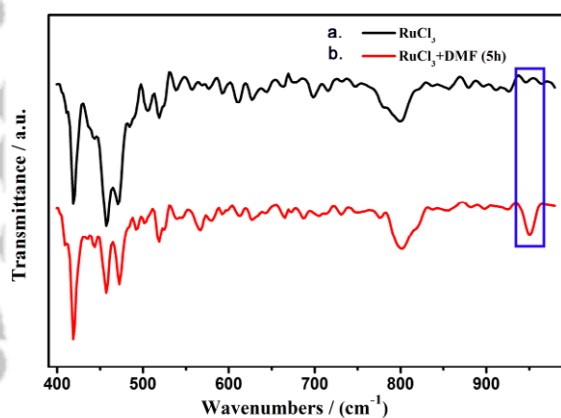
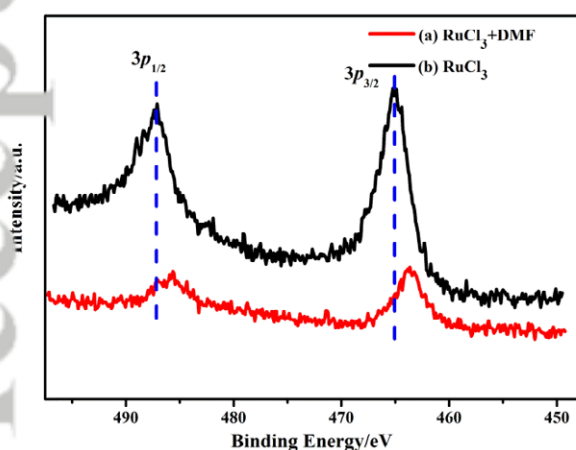


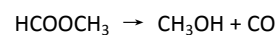
Fig. 3. IR spectra of the bending vibration peak of -OCN- group.

Fig. 4. IR spectra of amide absorption band of $\nu_{C=O}$.Fig. 5. IR spectra of (a) RuCl_3 , (b) $\text{RuCl}_3 + \text{DMF}$.Fig. 6. Ru 3p XPS spectra of (a) RuCl_3 coordinated with DMF and (b) RuCl_3 .

3) Exploration effect of promoters

We find that RuCl_3 -[PPN]Cl- Et_4NI catalyst system present a high-performance for the synthesis of MP from MF and ethylene. However, in entry 1, using RuCl_3 as catalyst without any promoter, the conversion of MF is 50.9% and the selectivity to MP is only 38.2%. From Fig. S2 and Fig. S3, there is more methanol of liquid products using RuCl_3 catalyst than RuCl_3 -[PPN]Cl- Et_4NI catalyst system. We proposed that part of the MF is decomposed without adding any promoter.

Based on the reported literature, we know MF may decompose to CH_3OH and CO , and the corresponding reaction is as follows:^[32]



CO is the breakdown product of MF. In order to investigate process of MF decomposition, different amount of CO is added in our high-performance RuCl_3 -[PPN]Cl- Et_4NI catalyst system (in Table 4). Interestingly, when introducing 0.3 MPa CO , the conversion of MF (39.3%) and selectivity to MP (3.66%) drop greatly. Further increasing the amount of CO (1.3 MPa), the conversion of MF decreases to 23.0% and the selectivity to MP decreases to 2.34% (entry 18), indicating that the presence of CO indeed limits the conversion of MF and the forming of MP, which may be that CO is able to coordinate with Ru compound making intermediate A inactivated. Compared the RuCl_3 and RuCl_3 -[PPN]Cl- Et_4NI catalyst systems, we deduce that promoters may restrain MF to decompose lead to high conversion of MF and high selectivity to MP.

Table 4. Exploration effect of promoters on MF decomposition.

entry	Catalyst	Promoter1	Promoter2	CO (MPa)	Conversion (%)	Selectivity (%)	Yield(%)
1	RuCl_3	-	-	-	50.9	38.2	19.4
5	RuCl_3	[PPN]Cl	Et_4NI	-	93.9	90.9	85.4
17	RuCl_3	[PPN]Cl	Et_4NI	0.3	39.3	3.66	1.44
18	RuCl_3	[PPN]Cl	Et_4NI	1.3	23.0	2.34	0.54

Experimental conditions: 16.3 mmol MF and 2.5 MPa ethylene, 0.019 mmol RuCl_3 , 0.008 mmol [PPN]Cl, 0.032 mmol Et_4NI , reaction temperature = 165 °C, reaction time = 5 h.

Developing a high-performance inorganic RuCl_3 -Nal catalyst system

Based on the results of Table 3, Et_4NI plays a more valuable role than [PPN]Cl in DMF at 165 °C, 2.5 MPa. A series of experiments were carried out about the effects of Et_4NI . As shown in Table 5, Et_4NI as a promoter has a great effect on reaction performance of synthesizing MP from MF and ethylene. Without the promoter Et_4NI , the conversion of MF and the selectivity to MP are 51.7% and 51.2%, respectively. As the amount of Et_4NI increases, the conversion of MF and the selectivity to MP are both enhanced gradually. When the additive amount of Et_4NI is 8.3 mg, the conversion of MF is high to 93.9%, the selectivity to MP reaches to 90.9%. Further increase the amount of Et_4NI , the conversion of MF further increases to 94.3%. However, the selectivity to MP decreases to 79.0%, suggesting that Et_4NI added in the reaction system can improve the conversion of MF and selectivity to MP, but the amount of Et_4NI is too large to well produce MP. The best amount of Et_4NI is 8.3 mg.

Although we obtain a high-performance $\text{RuCl}_3\text{-[PPN]Cl-Et}_4\text{NI}$ catalyst system (93.9% conversion of MF and 90.9% selectivity to MP), the catalyst system is still complex and adopt organic compounds as promoters ([PPN]Cl and Et_4NI), which increase the difficulty of further industrialization. In order to develop a simple catalyst system, we designed a series of experiments with different promoters.

As shown in Table 6, when adopting different promoters with the same anion (Cl^-), the yield of MP with Et_4NCl as a promoter (entry 26) is 75.2%, which is higher than that of [PPN]Cl (entry 28, yield: 33.3%) and NaCl (entry 27, yield: 28.4%) as a promoter. This suggests that cations indeed have a significant impact on the performance of this reaction and the performance order is $\text{Et}_4\text{N}^+ > [\text{PPN}]^+ > \text{Na}^+$, when adopting same anion (Cl^-). However, when adopting Et_4N^+ as cation, the yield of MP with Et_4NI as promoter (entry 25, yield: 77.4%) is higher than that of Et_4NCl (entry 26, yield: 75.2%), indicating that I^- as the anion may be inferior to Cl^- . Furthermore, to further confirm the role of I^- , we choose NaI (entry 29) as the promoter. Interestingly, the yield of MP using NaI as promoter is high to 86.7%, which is higher than that of NaCl (entry 27, yield: 28.4%), suggesting that the iodide is indeed the key component in promoters. Then, we performed the catalytic reaction with the KI promoter and the yield of MP is 71.7%. Based on the results of entry 26, 29 and 30 with the same anion (I^-), the yield order is $\text{Na}^+ > \text{Et}_4\text{N}^+ > \text{K}^+$, indicating that Na^+ is the better cation when adopting I^- as anion. Based on the above discussion, we know the reaction performance order is $\text{NaI} > \text{Et}_4\text{NI} > \text{KI} > \text{Et}_4\text{NCl} > [\text{PPN]Cl} > \text{NaCl}$. Anyway, as an inorganic compound, NaI is a better promoter.

And the yield of MP (86.7%) of $\text{RuCl}_3\text{-NaI}$ catalyst system is comparable with that of $\text{RuCl}_3\text{-[PPN]Cl-Et}_4\text{NI}$ catalyst system (85.4%), demonstrating that a high-performance inorganic catalyst system has developed successfully. Based on above discussion, we know the promoter can restrict the MF decomposition and be conducive to the formation of MP. Here, we also find that the amount of methanol produced by MF decomposition is very small and the amount of MP is very large (Fig. S4), indicating the NaI may inhibit the decomposition of MF and be beneficial to produce MP. Meanwhile, inorganic promoter NaI is conducive to the purification and separation of products.

The catalytic reaction is amplified by 1.5 times. The conversion of MF is 92.1%. The selectivity to MP is 83.1% indicating that the catalyst system is still good after amplification.

Table 5. The effect of Et_4NI on the synthesis of MP from MF and ethylene.

entry	$\text{Et}_4\text{NI}/\text{mmol}$	Conversion (%)	Selectivity (%)	Yield (%)
14	0.000	51.7	51.2	26.5
19	0.010	89.9	80.4	72.3
20	0.019	96.8	81.0	78.4
5	0.032	93.9	90.9	85.4
21	0.060	94.3	79.0	74.5
22	0.121	94.1	72.7	68.4
23	0.241	91.8	64.2	58.9
24	0.482	89.2	57.2	51.0

Experimental conditions: 16.3 mmol MF and 2.5 MPa ethylene, 0.019 mmol RuCl_3 , 0.008 mmol [PPN]Cl, reaction temperature = 165 °C, reaction time = 5 h.

Table 6. The effect of different promoters.

entry	Promoters	Conversion (%)	Selectivity (%)	Yield (%)
25	Et_4NI	91.2	84.9	77.4
26	Et_4NCl	96.7	77.8	75.2
27	NaCl	51.2	55.5	28.4
28	[PPN]Cl	62.3	53.4	33.3
29	NaI	88.8	97.6	86.7
30	KI	80.0	89.6	71.7

Experimental conditions: 16.3 mmol MF and 2.5 MPa ethylene, 0.019 mmol RuCl_3 , 0.040 mmol promoter, reaction temperature = 165 °C, reaction time = 5 h.

Reaction mechanism

Ru compounds have been employed because of well performance in C–H bond activation.^[10,33–40] Based on results of our experiments above, it is supposed that the reaction is conducted via catalytic cycle as Fig. 7. In the beginning, the active A species is oxidative addition by C–H bond of MF and to generate intermediate B. Subsequently, with promoters, ethylene inserts into Ru–H bond to form the ruthenium ethylmethoxycarbonyl species (intermediate C). Finally, the intermediate C undergoes the process of reductive elimination to produce MP by forming a new C–C bond and regenerate the active A species.

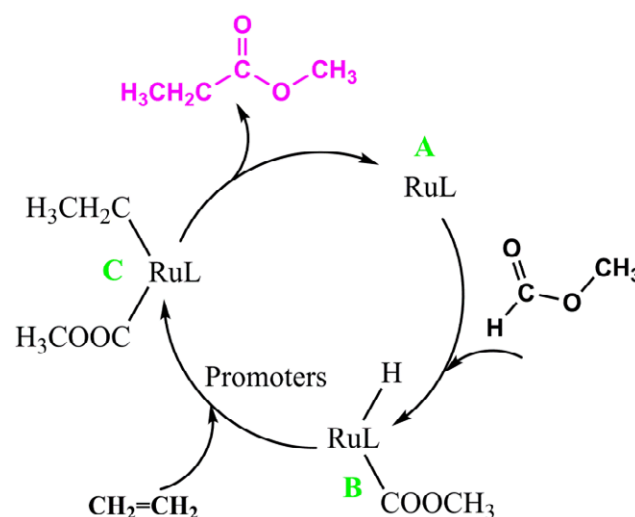


Fig. 7. The process of hydro-esterification of MF and ethylene.

Conclusions

In this work, a high-performance $\text{RuCl}_3\text{-[PPN]Cl-Et}_4\text{NI}$ catalyst system is first reported for this reaction. The conversion of MF and the selectivity to MP reach to 93.9% and 90.9%, respectively, at a mild reaction condition (165 °C, 2.5 MPa) by adopting DMF as solvent. However, promoters ([PPN]Cl and Et_4NI) are complex organic compounds, which increase the difficulty of studying reaction mechanism and further industrialization. Therefore, we further develop a high-performance inorganic catalyst system ($\text{RuCl}_3\text{-NaI}$). It is worth highlighting that the conversion of MF and selectivity to MP is 88.8% and 97.6%, respectively. And the yield of MP (86.7%) is comparable with that of $\text{RuCl}_3\text{-[PPN]Cl-Et}_4\text{NI}$ catalyst system (85.4%). NaI, as a promoter, may inhibit the decomposition of MF and be conducive to the formation of MP. Compared with promoters containing organic group, using inorganic promoter (NaI) is beneficial to the purification and separation of products. We hope that this work will re-arouse the attention to the reaction of MF and ethylene to MP.

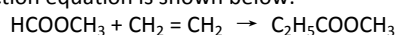
Experimental

Materials

Ruthenium trichloride (RuCl_3 , 99.5%), Tetraethylammonium iodide (Et_4NI , 99%), Bis(triphenylphosphine)iminium chloride ([PPN]Cl, 98%), Sodium chloride (NaCl, 99%), Sodium iodide (NaI, 99%), N,N-Dimethylformamide (DMF, 99.9%), n-Butanol (99.5%), Methylbenzene (99%), N,N-Diethylformamide (DEF, 99%), Formamide (99%), N-Methylformamide (NMF, 99%), Morpholine (99%), N,N-Dimethylacetamide (DMA, 99%). All above chemicals were purchased from Adamas-beta Co. Ltd.. MF (99%; Sigma-Aldrich Co. Ltd.), Ethylene (99.9%; Dalian Special Gases Co. Ltd), CO (99.99%; Dalian Special Gases Co. Ltd). All the chemicals were used as received without further purification.

Synthesis of MP from MF and ethylene

The reaction equation is shown below:



All reactions were carried out in stainless steel autoclaves (25 L inner volume). Evaluation process of catalyst is as follows. Firstly, the corresponding DMF, MF, RuCl_3 and promoters were added in the reactor and then sealed it. Secondly, ethylene was blown into the reactor several times to replace air. Then, 2.5 MPa ethylene was introduced into the reactor, and heated the autoclave under magnetic stirring. After reaction, the magnetic stirring was stopped and it was cooled to room temperature. The pure MP is obtained by vacuum distillation of products. The ^1H NMR spectra of MP is shown in Fig. S11.

The composition of liquid products was analyzed by a GC-2014 gas chromatograph (Shimadzu) equipped with a flame ionization detector (FID). The capillary column connected to the FID is composed with AE.FFAP fixation solution (50 m \times 0.15 mm \times 0.5 μm). Standard working curve method was adopted to achieve quantification in this work. The quantitative details were in part 7 of SI. In $\text{RuCl}_3\text{-NaI}$ catalyst system, the contained substances in

the reacted liquid are tested by GC chromatogram (in Fig. S8).

Acknowledgements

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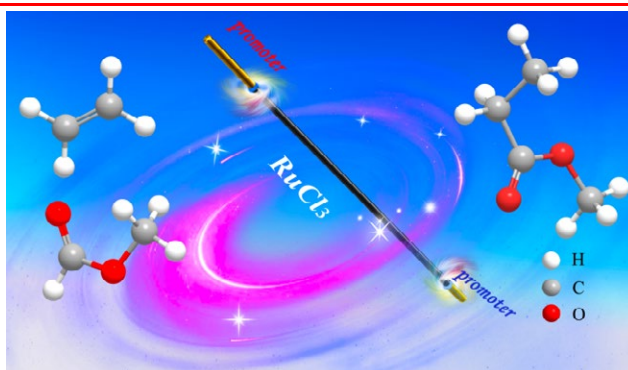
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High-performance RuCl_3 Catalyst Systems for Hydro-esterification of Methyl Formate and Ethylene



an-Ru Li, Zhong-Ning Xu, Bing Bai, Zhi-Qiao Wang,^a Guo-Cong Guo^b

High-performance RuCl_3 catalyst systems (RuCl_3 -[PPN]Cl- Et_4NI and RuCl_3 -NaI) have been developed for hydro-esterification of methyl formate and ethylene to methyl propionate.

^a Department, Institution, Address 1
E-mail:

^c Department, Institution, Address 3
E-mail:

^b Department, Institution, Address 2
E-mail: