The preparation and catalytic performance of novel amine-modified silica supported ruthenium complexes for supercritical carbon dioxide hydrogenation to formic acid

Yiping Zhang[a,b], Jinhua Fei[a], Yingmin Yu[a], and Xiaoming Zheng[a,*]
[a]*Institute of Catalysis, Xixi Campus, Zhejiang University, Hangzhou 310028, P.R. China*
[b]*Department of Chemistry, Zhejiang Education Institute, Hangzhou 310012, P.R. China*

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The three kinds of amine-modified silica supported ruthenium complexes developed for the first time are effective catalysts for the synthesis of formic acid from supercritical carbon dioxide and hydrogen, the activity is comparable to that of homogeneous catalysts, TOF up to 1190 h^{-1} can be obtained at 100% selectivity of formic acid over "Si"—NH_2—$RuCl_3$ with bis(1,2-diphenylphosphino)ethane used as ligand. These catalysts also offer the practical advantages such as easy separation and reuse.

KEY WORDS: ruthenium; supported; silica; formic acid; supercritical CO_2.

1. Introduction

The formation of formic acid and its derivatives such as methyl formate and *N*,*N*-dimethylformamide from catalytic hydrogenation of carbon dioxide are received special attention recently [1–3]. The homogeneous catalysts have been investigated to be effective for the reaction and ruthenium complexes were found to exhibit high activity. Performing this reaction in supercritical carbon dioxide ($scCO_2$) can obtain higher yields and rates of reaction, for example, the yield of formic acid reaches turnover number (TON) of 1400, the rate of reaction reaches turnover frequency (TOF) of 1400 h^{-1}, with $P_{H_2/CO_2}(atm) = 80/130$ [3], while TON of 264, TOF of 22 h^{-1} reported in a liquid solvent with $P_{H_2/CO_2}(atm) = 20/20$ [4], because hydrogen is highly soluble in supercritical phase. However, homogeneous catalysis is generally connected with the problem of separation from the reaction mixture, and the complexes are sensitive to air. These problems might be overcome by using the technique of immobilization of homogeneous catalyst. The group of Baiker employed sol–gel derived silica matrix supported $RuCl_2[P(CH_3)_3]_4$ as catalyst for the synthesis of *N*,*N*-dimethylformamide (DMF) from CO_2, H_2 and $NH(CH_3)_2$, giving a TOF of 1860 h^{-1} [5–7]. The catalyst was prepared by the co-condensation of $RuCl_2[P(CH_3)_2(CH_2)_2Si(OC_2H_5)_3]_3$ with $Si(OC_2H_5)_4$. They also synthesized a mesoporous ruthenium silica hybrid aerogel containing bidentate $RuCl_2[Ph_2P(CH_2)_3PPh_2]_2$ complexes using the sol–gel method, affords TOF up to 18,400 h^{-1} from CO_2, H_2 and $NH(CH_2CH_3)_2$ for the formation of *N*,*N*-diethylformamide [8].

In this paper we report the formation of formic acid from hydrogenation of carbon dioxide under supercritical condition, employing three kinds of amine-modified silica supported ruthenium complexes as catalysts.

2. Experimental

2.1. Preparation of catalysts

In a typical surface modification process, a mixture of fumed silica (6 g), anhydrous toluene (140 mL) and γ-aminopropyl triethoxysilica (4.65 g) was refluxed for 8 h, then 20 mL H_2O was added. The mixture was stirred again for 4 h. The organic silica ("Si"—NH_2) was filtered, and then dried in vacuum at 200 °C for 5 h.

A mixture of $RuCl_3 \cdot 3H_2O$ (0.035 g), "Si"—NH_2(1 g) and ethanol (32 mL) was stirred at room temperature for 1 h. The product was filtered, washed with ethanol, and dried in air, resulting the amine-modified silica supported ruthenium ("Si"—NH_2—$RuCl_3$).

Three kinds of method were used in the preparation of amine-modified silica supported ruthenium complex catalysts. The catalysts of method 1 were prepared as follows: using the "Si"—NH_2—$RuCl_3$ as catalyst precursor, and in the presence of phosphine ligands or in the presence of triphenylphosphine and sodium borohydride, ruthenium–phosphine complexes were formed in the process of CO_2 hydrogenation. These catalysts synthesized *in situ* were symbolized for "Si"—NH_2—$RuCl_3$ + phosphine ligand and "Si"—NH_2—$RuCl_3$ + PPh_3 + $NaBH_4$.

We also treated "Si"—NH_2—$RuCl_3$ with triphenylphosphine or triphenylphosphine and sodium borohy-

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* To whom correspondence should be addressed.
E-mail: xmzheng@dial.zju.edu.cn

dride as a reductant successively before the reaction of CO_2 hydrogenation, giving the immobilized ruthenium complexes of method 2, we marked them as "Si"—NH_2—$RuCl_3$—PPh_3 and "Si"—NH_2—$RuCl_3$—PPh_3—$NaBH_4$, respectively.

In the preparation of the catalysts of method 3, ruthenium complex was synthesized beforehand and then supported on amine-modified silica (identified as "Si"—NH_2—$RuCl_2(PPh_3)_3$, "Si"—NH_2—$RuH_2(CO)(PPh_3)_3$).

The ruthenium contents in the above-mentioned catalysts were measured by ICP instrument, varied in the range of 0.2×10^{-2}–0.6×10^{-2} g/g catalyst.

2.2. Catalytic reaction

The hydrogenation of CO_2 was carried out in a stainless steel autoclave. In a typical run, the immobilized catalyst (0.6 g), solvent (ethanol, 20 mL), and base (triethylamine, 5 mL) were added into the autoclave. The vessel was flushed with H_2 three times to remove air and was pressurized up to 4.0 MPa with H_2. Then the liquid CO_2 was pumped into the autoclave from a cooled (−5 °C) reservoir using a syringe pump to give the desired pressure. The vessel was heated to the reaction temperature (80 °C), the pressure was 16.0 MPa after temperature equilibration. Under these conditions, CO_2 is in the supercritical region. Although the reaction was performed in $scCO_2$, the system contains also other components: the solid catalyst, a vapor and a liquid phase. A large amount of CO_2 and dissolved H_2 were present in the liquid phase, which was the phase that the reaction occurred. And the reaction was stirred for the desired reaction time (1 h).

At the end of the reaction period, the reactor was cooled rapidly and vented carefully. Analysis of the gas phase by gas chromatography (GC) confirmed that no gaseous by-products (CO, CH_4) were formed. For all of the reactions in which base was added, almost no ethyl formate could be detected in the reaction solution, suggesting that the formic acid produced in the liquid might have formed a formate salt, consequently the reaction solution collected was acidified and the formic acid was esterified completely for analysis. The liquid sample was analyzed both by GC with FID detector using porapak Q column and gas chromatography–mass spectrography (GC–MS) using TC-wax column. The results of these two analytical methods agreed quite well.

3. Results and discussion

The catalytic results using the various immobilized catalysts and various ligands are presented in following tables.

Table 1 lists the catalytic results obtained with the various ruthenium immobilized catalysts for the synthesis of formic acid. "Si"—NH_2 and "Si"—NH_2—$RuCl_3$ tested as references exhibited no catalytic activity. Comparing the different preparation method of ruthenium immobilized catalysts, we found the activity, expressed as TOF, decreased in the order: method 1 > method 3 > method 2. The activity of catalysts synthesized *in situ* were about 2 times more than the catalyst prepared by method 2. The catalyst prepared by method 3 showed only moderate activity.

To *in situ* system referred to as method 1, the catalytic activity changed, depending on the ligand used during the CO_2 hydrogenation as showing in table 2. It can be found that the catalyst using phosphonic ligand (entry 1) exhibited higher activity than those using nitrogenous (entry 6) or arsenical ligand (entry 7). In addition, using bidentate phenyl phosphine ligands (entry 4, 5) instead of triphenylphosphine resulted in an even higher TOF, for example, TOF 1190 h^{-1} of dppe used as ligand, which is almost 2 times higher than that of triphenylphosphine used as ligand (656 h^{-1} of TOF). We can also observed from table 2 that when triphenylphosphine was used as ligand, the catalyst synthesized *in situ* with sodium borohydride as a reductant shows the highest activity (TOF 725 h^{-1}), while the addition of an oxidative triphenyl phosphine oxide suppressed the

Table 1
The activity of ruthenium catalysts using three kinds of immobilized method in $scCO_2$ hydrogenation[a]

Method	Catalyst	HCOOH (mmol)	TOF* (h^{-1})[b]
	"Si"—NH_2	0	0
	"Si"—NH_2—$RuCl_3$	0	0
1	"Si"—NH_2—$RuCl_3$ + PPh_3	13.12	656
	"Si"—NH_2—$RuCl_3$ + PPh_3 + $NaBH_4$	14.50	725
2	"Si"—NH_2—$RuCl_3$—PPh_3	6.36	318
	"Si"—NH_2—$RuCl_3$—PPh_3—$NaBH_4$	6.98	349
3	"Si"—NH_2—$RuCl_2(PPh_3)_3$	9.10	455
	"Si"—NH_2—$RuH_2(CO)(PPh_3)_3$	11.23	562

[a] Reaction conditions: reaction temperature = 80 °C; P[H_2] = 4.0 MPa, total pressure = 16.0 MPa; reaction time = 1 h.
[b] TOF = turnover frequency, mol of formic acid/mol of ruthenium/h.

Table 2
The effect of ligand on the activity of immobilized ruthenium catalysts in $scCO_2$ hydrogenation[a]

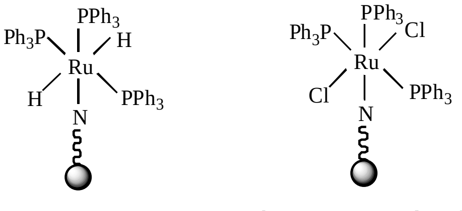
Entry	Method	Catalyst	HCOOH (mmol)	TOF (h^{-1})
1	1	“Si”—NH_2—$RuCl_3$ + PPh_3	13.12	656
2		“Si”—NH_2—$RuCl_3$ + PPh_3 + $NaBH_4$	14.50	725
3		“Si”—NH_2—$RuCl_3$ + $Ph_3P{=}O$	10.69	535
4		“Si”—NH_2—$RuCl_3$ + dppe[b]	23.80	1190
5		“Si”—NH_2—$RuCl_3$ + dppb[c]	18.07	904
6		“Si”—NH_2—$RuCl_3$ + NPh_3	2.67	134
7		“Si”—NH_2—$RuCl_3$ + $AsPh_3$	4.88	244
	2	“Si”—NH_2—$RuCl_3$—PPh_3	6.36	318
		“Si”—NH_2—$RuCl_3$—PPh_3—$NaBH_4$	6.98	349

[a] Reaction conditions: reaction temperature = 80 °C, $P[H_2]$ = 4.0 MPa, total pressure = 16.0 MPa, reaction time = 1 h.
[b] The ligand dppe = bis(1,2-diphenylphosphino)ethane, formula $Ph_2P(CH_2)_2PPh_2$.
[c] The ligand dppb = bis(1,4-diphenylphosphino)butane, formula $Ph_2P(CH_2)_4PPh_2$.

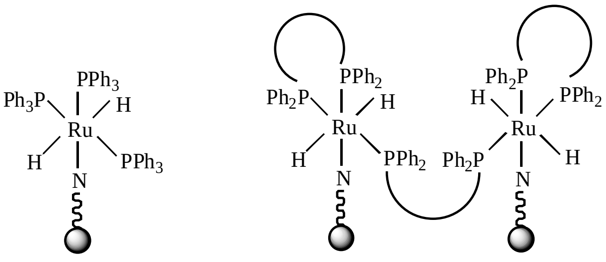
reaction (TOF 535 h^{-1}), it suggested that the trend in activity follows the same trend of the reducing property of the system. This conclusion was consistent with the data of the catalysts of method 2.

To study the relationship between the structure and the performance of the catalyst, we use infrared spectrometry (IR) and X-ray photoelectron spectrometry (XPS) to characterize the catalysts prepared by methods 1 and 2. The binding energy value due to Ru(3d 5/2) and N(1s) of XPS study indicated a coordinate bond of Ru—N was formed on the immobilized catalysts. To the catalysts of method 2, the bands at 1968 and 1910 cm^{-1}, which were assigned to Ru—H bond [9], appeared on “Si”—NH_2—$RuCl_3$—PPh_3—$NaBH_4$ in IR spectra, and there was no peak due to Cl(2p) in the XPS spectra. It indicated the structure of “Si”—NH_2—$RuCl_3$—PPh_3—$NaBH_4$ might be that shown in scheme 1a. The bands at 1968 and 1910 cm^{-1} were not found in the IR spectra of “Si”—NH_2—$RuCl_3$—PPh_3, and the presence of peak due to Cl(2p) in the XPS spectra indicated the structure of “Si”—NH_2—$RuCl_3$—PPh_3 might be that shown in scheme 2b. To the catalysts of method 1, the bands at 1968 and 1910 cm^{-1} can be found in the IR spectra, and there was no peak due to Cl(2p) in the XPS spectra to the catalyst filtered after reaction, so the structures of catalysts synthesized *in situ* were considered to be that shown in scheme 1c and d. Further efforts of characterization will be needed to confirm the formation of immobilized Ru complexes.

Over reused “Si”—NH_2—$RuCl_3$ + PPh_3 catalyst, which was separated from the liquid product by filtration, the activity dropped (see figure 1) when the recycle was occurred in the absence of phosphine ligand under the same reaction condition as that of fresh catalyst. In the process of separation, the catalyst was lost inevitably, but the ruthenium content in the recycled



a: "Si"-NH_2-$RuCl_3$-PPh_3-$NaBH_4$ b: "Si"-NH_2-$RuCl_3$-PPh_3



c: "Si"-NH_2-$RuCl_3$ + PPh_3 d: "Si"-NH_2-$RuCl_3$ + $Ph_2P(CH_2)_xPPh_2$

Scheme 1. The structures of immobilized catalysts prepared by methods 1 and 2.

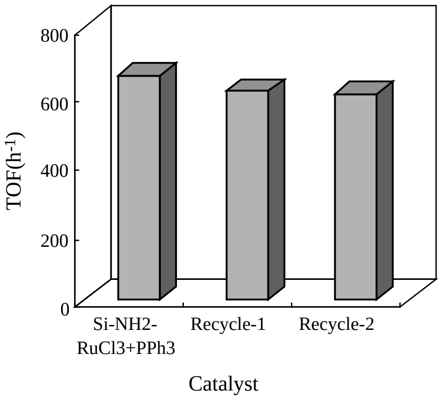


Figure 1. The activity of recycled immobilized ruthenium catalysts in $scCO_2$ hydrogenation.

catalyst measured by ICP instrument indicated that the drop of ruthenium from amine-modified silica was almost negligible, we believe that the drop of the activity is not due to the catalyst itself, but to the loss of catalyst in the separation process.

To prove this, the definitive test for no leaching was done as Sheldon noted [10]. The filtrate collected at reaction temperature was used to react further, it exhibited no activity within 24 h. So the observed catalysis is truly heterogeneous catalysis.

It is worthy noting that there was no formic acid formed in the absence of triphenylphosphine ligand to the fresh catalyst, but formic acid could be obtained in the absence of phosphine ligand in the recycle, probably attributed to the formation of the complex on the amine-modified silica supported ruthenium and phosphine ligand under reaction conditions in the first run.

4. Conclusion

The three kinds of amine-modified silica supported ruthenium complexes are not only effective catalysts for the synthesis of formic acid from supercritical carbon dioxide and hydrogen, but also offer the practical advantages such as easy separation and reuse.

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