

Water-Soluble Trialkylphosphine-Ruthenium(II) Complexes as Efficient Catalysts for Hydrogenation of Supercritical Carbon Dioxide

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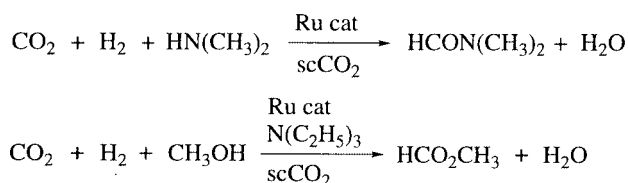
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A water-soluble ruthenium(II) complex bearing tris(hydroxymethyl)phosphine, $\text{RuCl}_2[\text{PH}(\text{CH}_2\text{OH})_2]_2\text{P}(\text{CH}_2\text{OH})_3]_2$, is highly effective for the catalytic hydrogenation of supercritical carbon dioxide (scCO_2) under $\text{scCO}_2\text{-H}_2\text{O}$ multi-phasic conditions.

Hydrogenation of CO_2 has been extensively investigated as a potential alternative method for synthesis of formic acid and its derivatives from toxic CO and alcohol or amine (Scheme 1).¹ Since we have achieved a rapid hydrogenation of scCO_2 ,^{2,3} catalyzed by a CO_2 -soluble Ru(II) complex with monodentate phosphine ligands, $[\text{RuCl}_2\{\text{P}(\text{CH}_3)_3\}_4]$ (**1**), there have been a number of reports on further progress in catalyst precursors demonstrated by Baiker's group.⁴ This CO_2 hydrogenation was characterized by an extremely high initial rate of reaction and high product selectivity as well as operational simplicity due to scCO_2 acting as a reactant and a unique reaction medium. In fact, complex **1** gave DMF with a high turnover number (TON) and in 99% selectivity albeit around 30% conversion based on the initially charged dimethylamine after 40 h.⁵ The coexisting amine plays an important role for overcoming the thermodynamically unfavourable addition of H_2 to CO_2 and its amount was known to have strong effect on the rate of the CO_2 hydrogenation. However, it should be required for a practical synthesis of DMF to achieve high amine conversion. These results prompted us to reinvestigate the catalytic performance of homogeneous and heterogeneous catalyst precursors for DMF synthesis via CO_2 hydrogenation under supercritical conditions. Now, we will describe the effect of water on DMF formation via CO_2 hydrogenation and the improvement in the catalyst's performance by using water-soluble Ru complexes with OH-substituted phospho-

Scheme 1.



rus ligands.

We first examined the reaction using CO_2 and H_2 in the presence of ammonium carbamate (8 mmol, $[(\text{CH}_3)_2\text{NH}_2]^+[\text{OCON}(\text{CH}_3)_2]^-$),⁶ catalyzed by the complex **1** (1.6 mmol, amine/catalyst = 10000) under H_2 (84–86 atm) and CO_2 (128–130 atm) at 100 °C for varying the reaction time. Table 1 summarizes the outcome of the reaction with catalyst **1** as a function of reaction time. It shows that the reaction was strongly retarded at the later stages, resulting in incomplete conversion

Table 1. Hydrogenation of scCO_2 by the Ru catalyst and the effect of the addition of H_2O into the catalyst system

Run	Cat	$\text{H}_2\text{O}/\text{amine}$	Time /h	TON	
				$[\text{NMe}_2\text{H}_2][\text{HCOO}]$	HCONMe_2
1	1	0	4	500	6900
2	1	0	16	0	7500
3	1	0	64	0	9600
4	1	0.5	4	1700	3600
5	1	2.0	4	470	240
6	2	0	4	1200	6200
7	2	0	48	0	10000
8	2	0.5	4	3100	4900
9	2	2.0	4	1500	4700

The reaction was conducted at 100 °C, in a 50-mL reaction vessel containing 1.6 mmol of $[\text{RuCl}_2\{\text{P}(\text{CH}_3)_3\}_4]$ (**1**) or $\text{RuCl}_2[\text{PH}(\text{CH}_2\text{OH})_2]_2[\text{P}(\text{CH}_2\text{OH})_3]_2$ (**2**), P_{H_2} = 84–86 atm, total initial pressure 216–220 atm. $[\text{NMe}_2\text{H}_2][\text{OCONMe}_2]:\text{Ru cat}$ = 5000:1.

based on the amine used under the tested conditions (Run 1–3).⁷

One of the possible reasons for the serious retardation is an inhibition of the H_2O coproduct which is formed in the dehydration of ammonium formate intermediate to DMF.⁸ We have previously reported the effect of water on the hydrogenation of CO_2 at 50 °C.^{5b} Although an addition of a small amount of water (0.1 mmol) accelerated the reaction, the rate of the reaction in the presence of a large amount of water which precipitates to form a liquid phase dropped drastically because of a phase separation giving a scCO_2 –liquid two phase system. Similarly, a significant drop in the rate of DMF synthesis for the initial 4 h was observed in the presence of a large amount of water (amine:water = 1:2, the ratio corresponds to the situation at 67% conversion based on the amine) as shown in Run 5 in Table 1. Visual inspection through sapphire view windows of a 50-mL high-pressure reactor confirmed that the ammonium carbamate (4 mmol) and H_2O (8 mmol) were precipitated as a liquid phase under the reaction condition. The liquid phase remained even in the presence of CO_2 -soluble DMF (8 mmol). Since a hydrous phase containing amine and/or ammonium carbonates (possibly formed from the reaction of amine, CO_2 and H_2O) does not merge with scCO_2 , a supercritical single-phase hydrogenation could not be performed leading to a significant loss in catalytic activity.^{5,9}

As an approach to suppression of catalytic deactivation caused by phase separation due to the formation of H_2O , we

examined the reaction catalyzed by a combination of $[\text{RuCl}(\text{cod})]_n$ (COD = 1,5-cyclooctadiene) with several water-soluble phosphine ligands in the place of $\text{P}(\text{CH}_3)_3$ under the similar conditions. Screening tests revealed as shown in Table 2 that water-soluble trialkylphosphine ligands containing OH groups¹⁰ such as $\text{P}(\text{CH}_2\text{OH})_3$ or $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_3$ were highly effective for the present hydrogenation rather than the well-known water-soluble triarylphosphine ligands, TPPTS and TPPMS.¹¹ The low activity of the triarylphosphines is consistent with the previously reported results that a conventional $\text{P}(\text{C}_6\text{H}_5)_3$ -based catalyst $\text{RuH}_2[\text{P}(\text{C}_6\text{H}_5)_3]_4$ is less active than the $\text{P}(\text{CH}_3)_3$ complex.^{5b} A ligand exchange reaction of $[\text{RuCl}_2(\text{cod})]_n$ with 4 mol amount of $\text{P}(\text{CH}_2\text{OH})_3$ in acetone solution affords $\text{RuCl}_2[\text{PH}(\text{CH}_2\text{OH})_2]_2[\text{P}(\text{CH}_2\text{OH})_3]_2$ (**2**), which has been structurally characterized by Higham et al.,¹² and hence the isolable complex **2** was used as a catalyst precursor in

Table 2. Hydrogenation of scCO_2 by Ru catalysts with water-soluble phosphines

Run	Phosphines	TON	
		$[\text{NMe}_2\text{H}_2][\text{HCOO}]$	HCONMe_2
1	none	<100	700
2	$\text{P}(\text{CH}_2\text{OH})_3$	300	7000
3	$\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_3$	100	5500
4	$\text{P}[3-(\text{SO}_3\text{Na})\text{C}_6\text{H}_4]_3$ (TPPTS)	<100	1900
5	$\text{P}(\text{C}_6\text{H}_5)_2[3-(\text{SO}_3\text{Li})\text{C}_6\text{H}_4]$ (TPPMS)	0	1100

The reaction was conducted at 100 °C for 16 h, in a 50-mL reaction vessel containing 1.6 mmol of $[\text{RuCl}_2(\text{cod})]_n$, p_{H_2} = 84–86 atm, total initial pressure 216–220 atm. $[\text{NMe}_2\text{H}_2][\text{OCONMe}_2]$:phosphine:Ru cat = 5000:4:1.

the following experiments.

The water-soluble complex **2** showed a considerable resistance to catalyst deactivation by H_2O as shown in Table 1. In the case of the addition of twice as much H_2O as amine, TONs of 1500 and 4700 for dimethylammonium formate and DMF (Run 9) were obtained with **2**, far greater than those with the $\text{P}(\text{CH}_3)_3$ complex **1** (vide supra). The remarkable advantage using the water-soluble catalyst **2** can be demonstrated by the complete conversion of the reaction of H_2 , CO_2 , and the ammonium carbamate into DMF after 48 h (Run 7). These results clearly show that the catalyst **2** effected the hydrogenation of CO_2 in a mixture of scCO_2 and H_2O leading to high catalyst performance in terms of reactivity and catalyst life time. The hydrophilic catalyst **2** also improves the hydrogenation of scCO_2 in the presence of methanol to a mixture of formic acid and methyl formate formed via esterification of formic acid giving H_2O (Scheme 1). The reaction catalyzed by **2** (methanol/catalyst = 10000) at 100 °C in the presence of $\text{N}(\text{C}_2\text{H}_5)_3$ as the base resulted in a higher total yield (TON = 1400) than that by **1** (TON = 200).

The phase behavior of the reaction mixture is crucial to the understanding of chemical reactions in supercritical fluids because the outcome of the reaction can be strongly affected by whether a particular catalysis system is single or multi-phasic.¹³ Phase separation often occurs during the progress of the reaction even if all components including the molecular catalysts, the starting materials, and the cosolvents are all soluble in

supercritical fluids at the initial stage of the reaction. The use of water-soluble trialkylphosphine ligands could overcome the catalyst deactivation encountered from the phase separation during the reaction.

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- The use of liquid dimethylammonium dimethylcarbamate is experimentally easier and more reproducible than cooled liquid dimethylamine. Both methods gave the same results.⁵⁾
- Baiker's catalyst $[\text{RuCl}_2(\text{dppe})_2]$ (DPPE = 1,2-bis(diphenylphosphino)ethane) showed a high initial TOF (turnover frequency: TON h^{-1}) exceeding 360000 h^{-1} at the initial 18% conversion based on dimethylamine.^{4a} However, no remarkable differences in the catalyst's performances between the $\text{P}(\text{CH}_3)_3$ -complex **1** and the DPPE complex were observed in our experiments.
- CO strongly inhibits the hydrogenation of CO_2 .^{5b} Complex **1** did not react with DMF at 100 °C to form less reactive carbonyl complexes.
- In water, direct hydrogenation of carbonate to formate is possible as reported by Joó et al. However, a much higher TON could be obtained even with the Ru-TPPMS complexes under our reaction conditions; F. Joó, G. Laurenczy, L. Nadasdi, and J. Elek, *Chem. Commun.*, **1999**, 971.
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