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An environmentally friendly hydroformylation using carbon dioxide as a reactant catalyzed by immobilized Ru-complex in ionic liquids

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Abstract

A mixed ionic liquid [bmim][Cl + NTf_2] system was successfully used as a reaction medium for Ru-catalyzed hydroformylation of 1-hexene with carbon dioxide in the absence of toxic CO and any volatile organic solvents. The yields and TONs are higher than those reported previously using conventional organic solvents. The product can be readily separated by distillation, and the reaction medium containing the Ru-catalyst was successfully recycled.

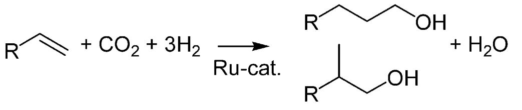
Keywords: Carbon dioxide; Hydroformylation; Ionic liquid; Ruthenium; Catalyst

1. Introduction

In the chemicals industry, in addition to traditional objectives such as productivity and cost, environmental considerations are now becoming important. According to the principles of green chemistry, a key approach for reducing pollutant emissions from chemical processes is pollutant prevention rather than treatment or clean up after they have formed [1]. The utilization of CO_2 as a reactant offers a route toward this goal since it is naturally abundant, nontoxic and inexpensive.

As an efficient route for producing aldehydes or alcohols, hydroformylation has become one of the most important processes in industry. Conventionally, the reaction has been carried out using metal complex catalysts in volatile organic solvents with highly toxic CO as a reactant.

With the aim of using CO_2 as an alternative to CO [2–8], we previously identified a new hydroformylation method catalyzed by ruthenium complexes using CO_2 as a reactant (Eq. (1)) [5–8]; this was the first hydroformylation using CO_2 as a reactant in place of CO.



(1)

Initially, the reaction was carried out in polar organic solvents such as *N*-methyl-2-pyrrolidone (NMP), however, although internal alkenes such as cyclohexene were effectively hydroformylated to give the corresponding alcohols in excellent yields, terminal alkenes were not because hydrogenation of the substrate occurred prior to hydroformylation [5,6]. This problem was overcome by applying a biphasic catalytic system using ionic liquids, which reduced unfavorable hydrogenation of the substrate and resulted in an increase in chemoselectivity toward hydroformylation [7,8]. Further, the catalyst species largely remained in the ionic liquid layer, which could be reused several times after separation of the produced alcohols with a simple extraction procedure. However, the previous catalytic systems still required volatile organic solvents. We now report an improved version of this catalysis: hydroformylation without the need for CO or any volatile organic solvents.

2. Experimental

All reagents and gases used in this study were chemical grade. $Ru_3(CO)_{12}$ was purchased from Strem and recrystallized

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before use. The following imidazolium salts were purchased from Solvent Innovation: [bmim]Cl (bmim: 1-butyl-3-methylimidazolium), [bmim]BF_4 and [bmim]PF_6. The chloride salt was purified by recrystallization and dried under a vacuum at room temperature overnight. Others were used after drying under a vacuum at 60 °C overnight. Although these salts took on a pale yellow hue even after the purification, they were used for the reaction experiments. $LiNTf_2$ was purchased from Kishida Chemicals and used as received. [bmim]NTf_2 was a colorless liquid prepared by anion exchange from [bmim]Cl and $LiNTf_2$ and dried under vacuum at 60 °C overnight [9]. The following chemicals were purchased from Wako Chemicals: toluene, *N*-methyl-2-pyrrolidone (NMP) and 1-hexene. Toluene and NMP were dried and purified by common methods while 1-hexene were used as received. GLC analyses were performed on a GL-Science GC-353 chromatograph with a FFAP capillary column (0.25 mm i.d. × 25 m). Products were identified with GC–MS analysis on a Shimadzu GCMS-5050A.

In a typical experiment, $Ru_3(CO)_{12}$ (0.1 mmol), [bmim]Cl (4.7 mmol), [bmim]NTf_2 (4.7 mmol) and 1-hexene (20.0 mmol) were placed in a 50 mL stainless steel autoclave. CO_2 (4.0 MPa) and H_2 (4.0 MPa) were introduced at room temperature. Then the reactor was heated to 160 °C and held at that temperature for 10 h with stirring. GC analysis showed that heptanol (16.4 mmol), hexane (1.7 mmol) and 1-hexene (1.2 mmol) were present in the liquid layer. The heptanol was isolated with Kugelrohr distillation (isolated yield = 70.1%).

3. Results and discussion

In this catalysis, the presence of halide salts is essential to activate CO_2 on the Ru-complex. The CO_2 conversion rate is known to increase in the order of $I^- < Br^- < Cl^-$, which corresponds to the order of halide proton affinity [4]. In this paper, all reactions were carried out in the presence of chloride salts.

Representative results of the reactions in various media are summarized in Table 1. When the reaction was carried out using only [bmim]Cl as an ionic liquid but without any volatile organic compounds other than the substrate (entry 1), the yield of heptanol was only 50.3%, which was much higher than the yield obtained by the previous reaction in NMP but lower than that by the toluene/[bmim]Cl biphasic system (entries 6 and 5). However, it is noteworthy that when half of the Cl^- anions were replaced with NTf_2^- anions (entry 2), the yield of heptanol was significantly increased to 82.0% and the TON (turnover number) reached over 160. Replacement with BF_4^- anions was also effective (entry 3), but the alcohol yield was slightly decreased. In contrast, replacement of the Cl^- anions with PF_6^- anions caused precipitation of unknown complexes and was inactive toward hydroformylation, as we previously reported (entry 4) [7].

Table 1
Ru-catalyzed hydroformylation of 1-hexene with CO_2 in various reaction media[a]

Entry	Reaction medium	Conversion (%)	Yield (%)		
			Heptanol	Heptanal	Hexane
1	[bmim]Cl	75.4	50.3	2.3	3.9
2[b]	[bmim][Cl + NTf_2]	94.0	82.0	0	8.5
3[b]	[bmim][Cl + BF_4]	95.2	71.0	0	9.1
4[b]	[bmim][Cl + PF_6]	93.5	49.5	0	6.5
5[c]	Toluene/[bmim]Cl	70.5	57.5	1.5	7.5
6[c]	NMP	99.5	17.5	0.5	48.0

[a] Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), ionic liquid (9.4 mmol), 1-hexene (20.0 mmol), CO_2 (4.0 MPa), H_2 (4.0 MPa), 160 °C, 10 h.

[b] The mole ratio of Cl:X = 1:1 (X = NTf_2, BF_4, PF_6).

[c] The amount of organic solvent was 5.0 mL.

The influence of reaction temperature was examined for the reaction using the mixed ionic liquid of [bmim][Cl + NTf_2]. As shown in Fig. 1, the optimum temperature for the hydroformylation lies at around 160 °C. At lower temperatures, the yield of heptanol was decreased due to a decrease in the reaction rate, whereas at higher temperatures, the hydrogenation of 1-hexene was enhanced, thereby decreasing the yield of heptanol. Even at lower temperatures, it is difficult to obtain heptanal selectively, since it is readily hydrogenated as it is formed to heptanol in the ionic liquid media.

The effect of the NTf_2^- anion was investigated as a function of its mol fraction in the ionic liquid layer (Fig. 2). As the Cl^- anions are replaced with NTf_2^- anions, the conversion of 1-hexene along with the yield of heptanol and hexane gradually increase. The yield of alcohol reaches a maximum when the mol fraction of NTf_2^- is about 0.5, and decreases with further replacement. Since the NTf_2^- anion is known to be relatively affinitive to organic substances among the ionic liquids [10], the increase in the conversion of 1-hexene and the yield of heptanol appear to be brought about by an increase in the solubility of 1-hexene. Similar correlation between the solubility of substrates in ionic liquids and reaction rates has been observed in other

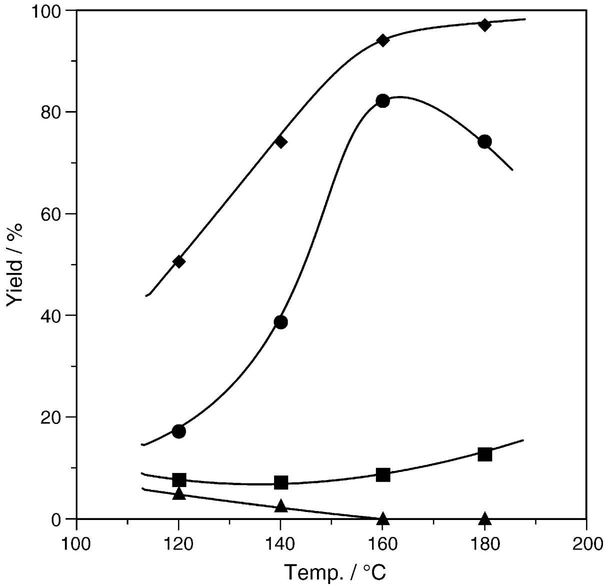

Fig. 1. Temperature dependency of the products distribution. Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), [bmim]Cl (4.7 mmol), [bmim]NTf_2 (4.7 mmol), 1-hexene (20.0 mmol), CO_2 (4.0 MPa), H_2 (4.0 MPa), 10 h. (◆) Conversion of 1-hexene, (●) yield of heptanol, (▲) yield of heptanal, and (■) yield of hexane.

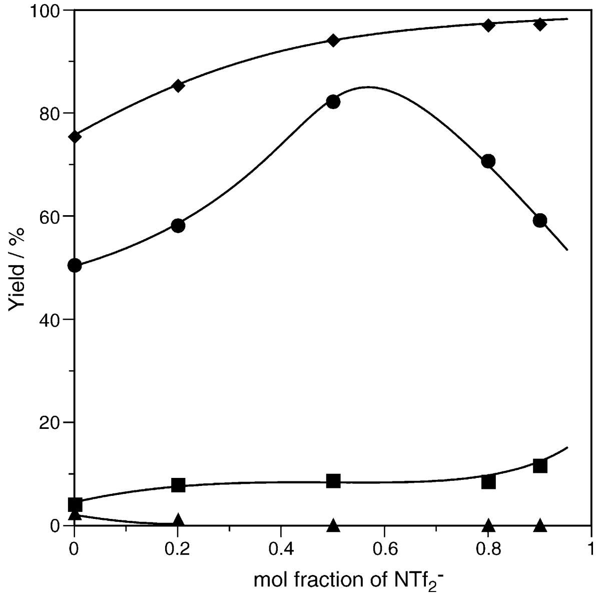

Fig. 2. The effect of the substitution of Cl^- with NTf_2^-. Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), ionic liquids (9.4 mmol), 1-hexene (20.0 mmol), CO_2 (4.0 MPa), H_2 (4.0 MPa), 160 °C, 10 h. (◆) Conversion of 1-hexene, (●) yield of heptanol, (▲) yield of heptanal, and (■) yield of hexane.

reactions [7,10]. However, further increase in the fraction of NTf_2^- brings about decrease in the yield of heptanol and a marked deficiency in the mass balance. This may be caused by aldol condensation of intermediately formed heptanal, which was also observed in the single-phased reaction using conventional organic solvents [6]. This result suggests that the biphase system may disappear at the early stage of the reaction under higher mole fraction of NTf_2^- because of its affinity for heptanol. Besides, the decrease in the yield of heptanol may also be affected by this anion being ineffective on the activation of CO_2.

Since this mixed ionic liquid is totally miscible with heptanol, distillation is the simplest and the most effective way to separate heptanol for this reaction. During the distillation, other organic substances and water can also be removed from the ionic liquid layer, which then can be used for the next run. A recycling experiment demonstrated that only a slight decrease in the catalytic activity was observed after five consecutive runs (Table 2).

Table 2
Recycling catalyst phase[a]

Run	Conversion (%)	Yield (%)		
		Heptanol	Heptanal	Hexane
1	94.0	82.0	0	8.5
2	98.0	75.0	0	11.5
3	97.0	78.0	0	16.0
4	97.5	77.5	0	13.5
5	96.5	75.5	0	13.5

[a] Conditions: $Ru_3(CO)_{12}$ (0.1 mmol), [bmim]Cl (4.7 mmol), [bmim]NTf_2 (4.7 mmol), 1-hexene (20.0 mmol), CO_2 (4.0 MPa), H_2 (4.0 MPa), 160 °C, 10 h.

In conclusion, immobilization of a Ru catalyst in a mixed ionic liquid [bmim][$Cl + NTf_2$] offers an effective alternative for carrying out hydroformylation, requiring only CO_2, H_2 and the substrate, without the need for toxic CO or any volatile organic solvents. In light of the higher catalytic activity and ease of recycling, this catalytic system is expected to contribute to more benign hydroformylation using CO_2.

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