SHORT PAPER

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Oxidative carbonylation of methanol to dimethyl carbonate in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate[†]

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The synthesis of dimethyl carbonate (DMC) by oxidative carbonylation of methanol with $PdCl_2$ as a catalyst was investigated in the room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). The products were recovered *in situ* using supercritical carbon dioxide. Enhanced selectivity of DMC over this catalyst was observed in the synthesis in [bmim][PF_6] compared with the situation without the ionic liquid (IL). The mixture of catalyst and [bmim][PF_6] could be recycled.

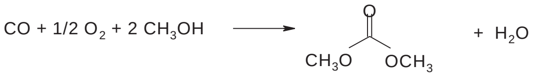
Keywords: ionic liquids, dimethyl carbonate, methanol, oxidative carbonylation

The use of volatile organic solvents is one of the sources of environment pollution. Chemists are attempting to eliminate the use of solvents or to use environmentally benign solvents in chemical reaction processes. Ionic liquids (ILs) are very attractive environmentally acceptable solvents because they have almost undetectable vapour pressure and are stable in a wide temperature range.[1-3] Recently, an increasing number of scientists are interested in reactions in ILs, and different reactions have been studied, such as Friedel–Crafts reactions,[4,5] alkylations,[6,7] hydrogenations,[8-10] hydroformylations,[11-13] Diels–Alder reactions,[14] Heck reactions,[15,16] olefin dimerisation and oligomerisation,[17,18] and oxidations.[19-21]

It was recently reported that supercritical CO_2 ($scCO_2$) is highly soluble in some ILs while the ILs are insoluble in $scCO_2$.[22] Studies also revealed that $scCO_2$ could extract many organic compounds from ILs.[22,23] This provides an opportunity to separate $scCO_2$-soluble chemicals from ILs using $scCO_2$ without any cross-contamination. This principle has been successfully applied to separate $scCO_2$-soluble products from the ILs in some reaction processes.[9-12,24]

DMC is a valuable compound with versatile chemical reactivity. It can be used as an environment-friendly intermediate substituting for phosgene in polycarbonate and isocyanate synthesis, and for dimethyl sulfate in various methylation reactions.[25] In addition, DMC is a potential gasoline fuel additive to enhance the oxygenate content.[26]

DMC has been produced from methanol and phosgene in concentrated sodium hydroxide solution. Extensive study has been conducted on alternative synthesis without using $COCl_2$. The method of oxidative carbonylation of methanol is one of the effective routes to produce DMC.[27-30] It is known that $PdCl_2$/$CuCl_2$/CuCl are active and most frequently used catalysts for the synthesis of DMC by oxidative carbonylation of methanol (Scheme 1).[31-33]



Scheme 1

Table 1 Effects of molar ratio of O_2/CO on oxidative carbonylation of methanol [a]

Molar ratio of O_2/CO	Selectivity of products /mol% DMC[b]	DMM[b]	Methanol conversion/%
13/87	13	87	2.1
20/80	13	87	4.2
29/71	25	75	6.8
50/50	6	94	6.0
29/71[c]	6	94	5.8

[a] Reaction conditions: temperature, 110°C; total pressure, 10 MPa; reaction time, 1 h; methanol, 50 mmol; palladium chloride, 0.04 mmol; [bmim][PF_6], 1.4 g.
[b] DMC = dimethyl carbonate; DMM = dimethoxy methane.
[c] Without the IL.

In this work, synthesis of DMC by the oxidative carbonylation of methanol using $PdCl_2$ as catalyst is carried out in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). The effects of temperature, pressure, molar ratios of O_2/CO, and reaction times on the selectivity are examined. The results are presented in Tables 1–5.

Table 1 lists the effect of molar ratio of O_2/CO on the oxidative carbonylation of methanol at a pressure of 10 MPa, as the content of O_2 in the gaseous mixture increases from 13% to 50%. The highest selectivity of DMC and methanol conversion is observed when the O_2 content is 29%.

At the molar ratio of O_2/CO 29/71, the effects of total pressure of O_2 and CO on oxidative carbonylation of methanol were studied. The results in Table 2 show that total pressure does not seem to affect the selectivity of DMC significantly in the pressure range of 8–12 MPa, but the conversion of methanol is lower at the low pressures.

As shown in Table 3, temperature has significant effect on the selectivity and conversion of the reaction. At the lowest temperature (70°C), very little methanol can be converted and the selectivity to DMC is extremely low. Both DMC selectivity and methanol conversion increase and then decrease with the raising of temperature. The highest selectivity to DMC and highest methanol conversion occur at about 110°C in the temperature range of 70–150°C.

Table 4 shows the effect of reaction time on the conversion of methanol and selectivity. The conversion does not change considerably with increasing time up to 4 h. However, the shorter reaction time favours the selectivity of DMC.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Effects of pressure on synthesis of DMC by oxidative carbonylation of methanol[a]

Total pressure MPa	Selectivity of products/mol%		Methanol conversion/%
	DMC	DMM	
8	17	83	2.3
9	20	80	2.7
10	25	75	6.8
11	22	78	6.6
12	22	78	4.5

[a]Reaction conditions: temperature, 110^{o}C; molar ratio of O_2/CO, 29/71; reaction time, 1 h; methanol, 50 mmol; Palladium chloride, 0.04 mmol; [bmim][PF_6], 1.4 g.

Table 3 Effect of temperature on oxidative carbonylation[a]

Reaction temperature/^{o}C	Selectivity of products/mol%		Methanol conversion/%
	DMC	DMM	
150	14	86	5.6
130	22	78	6.1
110	25	75	6.8
90	12	88	3.9
70	1	99	2.0

[a]Reaction conditions: total pressure, 10 MPa; molar ratio of O_2/CO, 29/71; reaction time, 1 h; methanol, 50 mmol; Palladium chloride, 0.04 mmol; [bmim][PF_6], 1.4 g.

Table 4 Effect of reaction time on oxidative carbonylation[a]

Temperature/^{o}C	Reaction time/h	Selectivity/ mol%		Methanol conversion/%
		DMC	DMM	
130	1	22	78	6.1
130	4	13	87	6.4
110	1	25	75	6.8
110	2	14	86	6.7
110	4	15	85	6.9

[a]Reaction conditions: total pressure, 10 MPa; molar ratio of O_2/CO, 29/71; methanol, 50 mmol; palladium chloride, 0.04 mmol; [bmim][PF_6], 1.4 g.

Table 5 Results for recycling of IL-catalyst system[a]

Recycle no.	Selectivity of products/mol%		Methanol conversion/%
	DMC	DMM	
1	21	79	6.2
2	22	78	6.0
3	17	83	6.3

[a]Reaction conditions: reaction temperature, 130^{o}C; other conditions are the same as Table 3.

The results for repeated conduction of the reaction are in Table 5. It is shown that the catalyst can be recycled for at least three times. After three successive runs, no significant drop on methanol conversion was observed, but the selectivity to DMC decreased slightly.

To explore the advantages for conducting the reaction in the IL, the reaction was also conducted in the absence of the IL (O_2/CO=29/71). The results are also given in Table 1. The data in the table indicate that the conversion of the reaction in the presence of the IL is larger than that without the IL, although a vapour/IL interface exists as the IL is used. The main reason is that the catalysts are well dispersed in the IL-rich phase, which is favourable to enhancing the reaction rate in the CO_2/IL system. On the other hand, the liquid/vapour interface is not favourable to increasing the reaction rate due to the interface mass transfer. The first factor is dominant, and thus the conversion is larger as the IL is used.

It is interesting that the selectivity of DMC in the presence of IL is much larger than that in the absence of the IL. We believe that the catalyst-solvent and solvent-reactant interactions may be favourable to producing DMC.

In summary, IL [bmim][PF_6] slightly increases the conversion of methanol and greatly enhances the selectivity of DMC in the process of oxidative carbonylation of methanol for synthesis of DMC catalysed by $PdCl_2$. The catalytic system ($PdCl_2$+IL) can be reused at least three recycles.

Experimental

[Bmim][PF_6] was synthesised according to the procedures reported in the literature.[34] 1-Methylimidzole (99% in purity) was used as received from ACROS ORGANICS. 1-Chloride-n-butane supplied by Beijing Chemical Reagent Factory was A.R. grade. The synthesised [bmim][PF_6] was dried under vacuum at 50^{o}C for about 48 h before use.

Both $PdCl_2$ and methanol were A.R. grade regents produced by the Beijing Chemical Regent Factory. O_2(>99.95%), CO(>99.95%), and CO_2(>99.95%) were supplied by the Beijing Analytical Instrument Factory.

In a typical reaction, [bmim][PF_6] (1.4 g), methanol (50 mmol), palladium (0.04 mmol) were added to a stainless steel reactor of 20 ml, and then the reactor was purged with O_2 several times. O_2 and CO was then introduced into the reactor via controlling the pressure. Finally, the reactor was put into a constant temperature air bath of desired temperature. After the reaction, the reaction mixture was released, passing the gases through a cold trap containing DMF, and the gas mixture was collected in a gasbag for GC analysis. The product left in the reactor was extracted *in situ* with CO_2 at 50 ^{o}C and 12.0 MPa. To conduct the recycling experiments, the IL-containing catalyst was reused without further purification after the extraction process.

GC (Agilent 4890D) with a FID and a TCD was used to analyse the product. Gas product was analysed with a package column of carbon sieve (1 m×3 mm) and the TCD, while the liquid product was analysed using an Innowax capillary column (30 m×0.252 mm× 0.25 µm) and the FID.

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