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Ionic liquid as an efficient promoting medium for synthesis of dimethyl carbonate by oxidative carbonylation of methanol

Wen-Sheng Dong *, Xianshu Zhou [1], Chunsheng Xin [1], Chunling Liu *, Zhaotie Liu

Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, Ministry of Education,
School of Chemistry and Materials Science, Xi'an 710062, PR China

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Abstract

The synthesis of dimethyl carbonate by oxidative carbonylation of methanol using Cu salt catalysts in the presence of various room temperature ionic liquids (RTILs) was reported. Among the ionic liquids used, *N*-butylpyridinium tetrafluoroborate was the most effective promoter in terms of the conversion of methanol and the selectivity to dimethyl carbonate (DMC). The influences of reaction temperature, pressure, time, molar ratio of CO/O_2, and amount of the ionic liquid on the oxidative carbonylation of methanol were investigated. The results indicated that under the reaction conditions of 120 °C and 2.4 MPa of a 2:1 mixture of CO and O_2, 17.2% conversion of methanol, 97.8% selectivity of DMC and a DMC productivity of 4.6 g g^{-1} cat h^{-1} were achieved. The *N*-butylpyridinium tetrafluoroborate-meditated CuCl catalyst system could be reused at least five recycles with the same selectivity and a slight loss of catalytic activity due to loss of the catalyst during handling and transferring the reaction mixture.

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1. Introduction

Dimethyl carbonate (DMC) is an environment-friendly building block for versatile chemical applications. It has been used as a non-toxic carbonylating and methylating agent to substitute for phosgene and dimethyl sulfate — two toxic and corrosive chemicals that industry has been trying to phase out [1–3]. The DMC technology may contribute to "Green Chemistry" by replacing toxic or high waste technology. In addition, DMC gained interest as a dipolar aprotic solvent and as a fuel additive that improves the octane number and that replaces more toxic or less biodegradable additives. Several reaction routes *e.g.* the phosgenation of methanol, methanol oxy-carbonylation, methylnitrite carbonylation, the transesterification of ethylene or propylene carbonate with methanol, methanol reaction with urea, methanol reaction with CO_2, *etc.* have been known for DMC production; among them, the one-step methanol oxidative carbonylation process is by far the most popular phosgene-free route for the industrial production of dimethyl carbonate [3–6].

The oxidative carbonylation process, based on a homogeneous reaction using cuprous chloride as catalyst, was first developed by EniChem in 1983. In recent developments of the EniChem technology, at 2.4 MPa and 130 °C a DMC productivity of 135 g l^{-1} h^{-1} was reported; values up to 250 g l^{-1} h^{-1} have been reached under optimized conditions [5]. However, one of the main drawbacks for this catalyst system is that cuprous chloride is sparingly soluble in methanol and as a result the reactants cannot react with the catalyst efficiently to form active intermediates. Moreover, cuprous chloride is highly corrosive to metallic vessels due to the existence of Cl^- and the redox reaction of Cu(I) [7]. In order to overcome such drawbacks, researchers have investigated various base additives *e.g.* amines and pyridines as promoters and co-solvents or immobilized copper salts on supports [8–17]. For example, Raab et al. [10] investigated the influence of *N*-donor ligands on the copper-catalyzed oxidative carbonylation of methanol, and found that catalyst

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* Corresponding authors. Tel.: +86 29 85303657; fax: +86 29 85303657.
E-mail addresses: wsdong@snnu.edu (W.-S. Dong), clliutt@yahoo.com.cn (C. Liu).

[1] These authors contributed equally for this article.

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complexes with three or four *N*-methylimidazole ligands at $Cu^{+}/^{2+}$ could increase both the conversion of methanol and the selectivity to DMC compared to the plain copper halides. Mo et al. studied the CuCl/Schiff base catalytic system in the synthesis of DMC by oxidative carbonylation of methanol. Their results indicated that the catalytic performance of CuCl was enhanced dramatically and the corrosion of the reaction system was effectively inhibited when 1,10-phenathroline was used as a ligand [11].

Recently, room-temperature ionic liquids (RTILs) with very low vapor pressure, high thermal stability, low viscosity, wide liquid range and an excellent ability to dissolve salts, metals and organic compounds have attracted a significant interest [17]. These characteristics make RTILs extremely useful reaction media, which are becoming increasingly important technologically. Numerous catalytic reactions that proceed in ionic liquids (ILs) have been reported, with excellent performances in many cases [18–22]. Synthesis of DMC by the oxidative carbonylation of methanol using $PdCl_2$ catalyst was also carried out in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [23]. However, the corresponding conversion of methanol and selectivity of DMC are rather low (6.8% and 25%, respectively), whereas the reaction pressure is too high (10 MPa). In the present work, the ionic liquid-mediated cuprous chloride catalyst system for the oxidative carbonylation of methanol to give corresponding DMC was investigated. The aim is to establish an effective catalytic system for the carbonylation of methanol through the selective dissolvability and special mediation of ionic liquid.

2. Experimental

2.1. Compounds and materials

The ionic liquids, [BPy]Cl (*N*-butylpyridinium chloride), $[BPy]BF_4$ (*N*-butylpyridinium tetrafluoroborate), $[BPy]PF_6$ (*N*-butylpyridinium hexafluorophosphate), $[OPy]BF_4$ (1-octylpyridinium tetrafluoroborate), [EMIm]Cl (1-butyl-3-methylimidazolium chloride), $[EMIm]BF_4$ (1-ethyl-3-methylimidazolium tetrafluoroborate), $[OMIm]BF_4$ (1-octyl-3-methylimidazolium tetrafluoroborate), $[OMIm]PF_6$ (1-octyl-3-methylimidazolium hexafluorophosphate), $[BDMIm]BF_4$ (1-butyl-2,3-dimethylimidazolium tetrafluoroborate) and $[BDMIm]PF_6$ (1-butyl-2,3-dimethylimidazolium hexafluorophosphate) were purchased from Chemer Company (Hangzhou, China); their purities are higher than 97%. Prior to use, the ionic liquids were dried under vacuum at 50 °C for about 24 h. Methanol, *n*-amyl alcohol, CuCl, $CuCl_2{\cdot}2H_2O$, $CuBr_2$, CuBr and CuI were A.R. grade regents and were used as received. O_2 (>99.99%) and CO (>99.99%) were supplied by the Xi'an MESSER Gas Company.

2.2. Reaction procedure

All reactions were conducted in a 25 ml stainless steel autoclave with a glass tube inside equipped with magnetic stirring. In a typical experiment, 1 mmol Cu catalyst, 2.0 g ionic liquid and 4.0 g methanol were added into the autoclave. The autoclave was then sealed tightly, purged three times with CO and then pressurized to 2.4 MPa with CO and O_2 ($p_{CO}/p_{O_2} = 2:1$) at room temperature. The reaction proceeded at 120 °C for 2 h. After the reaction, the reactor was cooled down to below 5 °C with an ice-water mixture and depressurized. The gas mixture was collected in a gasbag for GC analysis. An internal standard of *n*-amyl alcohol was added in the liquid product. Quantitative analysis was performed using an Agilent 6820 GC with an INNOWAX capillary column (30 m × 0.32 mm × 0.5 μm) and the FID.

Infrared spectra were recorded on a Nicolet 170 FTIR spectrometer using KBr disc technique.

3. Results and discussion

3.1. Comparison of ionic liquids

The results of preliminary screening of various ionic liquids as reaction media for the synthesis of DMC by oxidative carbonylation of methanol using CuCl catalyst are summarized in Table 1. The main byproducts in the oxidative carbonylation reaction of methanol were dimethoxymethane (DMM), dimethylether (DME) and methylformate (MF). In comparison with the results obtained in the absence of ionic liquids (entry 1), the catalytic efficiency and space–time yields (STY) could

Table 1
Oxidative carbonylation of methanol catalyzed with CuCl in ionic liquids

Entry	Ionic liquids	Conversion (%)	Selectivity of DMC (%)	Selectivity of DMM (%)	Selectivity of DME (%)	STY (g DMC g^{-1} cat h^{-1})
1	–	9.0	97.3	2.8	–	2.3
2	$[BPy]BF_4$	17.2	97.8	2.3	–	4.6
3	$[OPy]BF_4$	17.0	98.3	1.8	–	4.6
4	$[BDMIm]BF_4$	13.9	99.2	0	–	3.8
5	[BPy]Cl	14.2	87.0	0	9.7	3.5
6	[BMIm]Cl	4.3	70.3	5.3	25.8	0.8
7	$[EMIm]BF_4$	6.5	81.2	5.3	14.5	1.5
8	$[OMIm]BF_4$	9.1	93.5	2.4	4.5	2.3
9	$[BPy]PF_6$	5.4	32.4	9.1	58.5	0.5
10	$[OMIm]PF_6$	8.0	53.2	5.5	43.0	1.2
11	$[BDMIm]PF_6$	7.0	51.6	5.0	45.0	1.0

Reaction conditions: 120 °C; 2.4 MPa; $p_{CO}/p_{O_2} = 2:1$; 2 h; 1 mmol CuCl; 2.0 g $[BPy]BF_4$; 4.0 g CH_3OH.

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