



Short communication

Highly efficient synthesis of dimethyl carbonate from methanol and carbon dioxide using IL/DBU/SmOCl as a novel ternary catalytic system



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ABSTRACT

Excellent yield of dimethyl carbonate (DMC) was obtained by direct physical or chemical adsorption of carbon dioxide on [EmimOH][NTf₂] ionic liquid (IL) in the presence of samarium oxychloride (SmOCl) and 1,8-diazabicyclo[2.2.2]undec-7-ene (DBU) as a super base. The novel ternary catalyst system consisting of [EmimOH][NTf₂], DBU, and SmOCl was found to appreciably convert methanol (13.01%) to DMC with excellent selectivity (99.13%). The adsorption of CO₂ on IL in the presence of DBU was analyzed by ¹³C experiment. Moreover, catalytic reactivity of SmOCl and OH-functional group was proved by a predictable mechanism. Various parameters such as reaction temperature, pressure, reaction time, and reusability of catalyst were investigated to maximize DMC yield.

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1. Introduction

Carbon dioxide (CO₂) is a primary greenhouse gas produced by human activities. Because of its enormous emission, CO₂ contributes >60% to global warming [1]. On the contrary, CO₂ is an abundant non-toxic and recyclable carbon source that can substitute conventional toxic chemicals such as phosgene, isocyanides, and carbon monoxide [2]. Synthesis of carbonic acid esters has attracted considerable research attention recently. Dimethyl carbonate (DMC) is the lowest homology of this family, which has several industrial applications, including use as methylating [3] and carbonylating agent [4] instead of toxic dimethyl sulfate and phosgene, food-flavoring agent [5], solvent for secondary lithium-ion batteries [6], and reagent for biodiesel production [7].

Phosgenation was the first commercial method for the production of DMC, but due to the extreme toxicity of phosgene, this process has been replaced by processes such as oxidative carbonylation and transesterification. Major drawbacks of oxidative carbonylation are the use of poisonous and corrosive gases and explosion risk associated with the use of CO and O₂ mixture. On the contrary, direct synthesis of DMC from CO₂ and methanol could be an ideal alternative for DMC production at commercial level. The use of cheap, abundant, and non-corrosive raw materials (CO₂ and MeOH) makes it an environmentally benign process [8]. Although a number of catalysts such as Ni(acetate)₂, ZrO₂, polyphosphoric acid–ZrO₂, ZrO₂–MgO, CeO₂, and Ce–ZrO₂ solid solutions have been investigated for this reaction, DMC yield still remains low [9,10]. The use of stoichiometric amounts of dehydrating agents can help increase DMC yield considerably. However, most of

these agents are irrecoverable or require a regeneration process. Therefore, their use has some limitations in terms of production cost. In addition, DMC reaction also proceeded smoothly with high yield using catalyst including tin alkoxy compounds such as Bu₂Sn(OEt)₂, Sn(OMe)₄, and Sn(OBu)₄ [10].

In recent years, ionic liquids (ILs) have attracted increasing attention as catalyst due to their broad liquid range and excellent thermal and chemical stability [11,12]. Concentration of CO₂ in solution increased significantly by adding IL into the reaction mixture. In addition to being a CO₂ sorbent, ILs can act as a water scavenger. Therefore, their use as a solvent, promoter, or catalyst has been extensively investigated by several groups. In this study, basic IL is synthesized, whose combination with an organic super base, 1,8-diazabicyclo[2.2.2]undec-7-ene (DBU), can reversibly capture CO₂. The effect of addition of metal salts is also investigated. This ternary system consisting of an IL, organic base, and metal oxychloride was found to be highly efficient for catalyzing direct DMC synthesis.

2. Experimental

2.1. Preparation of IL

2.1.1. Preparation of 1-(2-hydroxyethyl)-3-methyl imidazolium chloride [EmimOH][Cl] IL

1-Methyl imidazole (10.0 g 0.12 mol) and 2-chloroethanol (14.7 g, 0.12 mol) were taken in a 100-ml round-bottomed flask and refluxed with 40-ml acetonitrile under continuous stirring for 28 h. Then, the reaction mixture was slowly cooled to –4 °C to afford a white crystalline solid as 1-(2-hydroxyethyl)-3-methyl imidazolium chloride IL.

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Table 1
Catalytic performance of various ILs for synthesis of DMC.

Entry	Catalyst/additive	Methanol conversion [%]	DMC selectivity [%]	Yield [%]
1	– ^a	–	–	–
2	DBU	1	2	0
3	[EmimOH][Cl]	14.3	33.7	4.8
4	[EmimOH][NTf ₂]	8.1	60.0	4.8
5	[EmimOH][NTf ₂] + DBU	9.5	72.2	6.9
6	[EmimOH][NTf ₂] + DBU + SmOCl	13.0	99.1	12.8

^a Reaction carried out without any catalyst. Reaction conditions: 783 mol of methanol, 6.4 MPa CO₂, 4 g IL, 1 g DBU, 4 h.

2.1.2. Preparation of 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl) imide [EmimOH][NTf₂] IL

1-(2-Hydroxyethyl)-3-methyl imidazolium chloride (6 g, 0.018 mol) was reacted with bis(trifluoromethanesulfonyl)imide lithium salt (10.6 g, 0.018 mol) and 40 ml of acetone under stirring at room temperature for 28 h. Then, the mixture was filtered to remove LiCl salt formed during the reaction. The filtrate was then evaporated under reduced pressure to obtain [HEMIm][NTf₂] IL, which was subjected to silver nitrate test to ensure complete removal of chloride.

2.2. Characterization

All synthesized ILs were characterized by ¹H nuclear magnetic resonance (NMR) and ¹³C NMR spectroscopy using Bruker 500 MHz and 125 MHz spectrometers, respectively, in CDCl₃. Infrared spectra of the prepared ILs were observed by a Fourier transform infrared

spectrum (FTIR, Varian 2000). Thermal decomposition temperature was measured using thermogravimetric analysis (TGA, PerkinElmer TGA-7 instrument). Differential scanning calorimetry (DSC) data were obtained in a sealed aluminum pan with a cooling and heating rate of 10 °C/min on Mettler DSC822. The general structure of the compounds was examined by X-ray diffraction (XRD) using an analytical X'Pert MPD diffractometer with Bragg's angle ranging from 20° to 80°.

2.3. DMC synthesis from methanol and CO₂

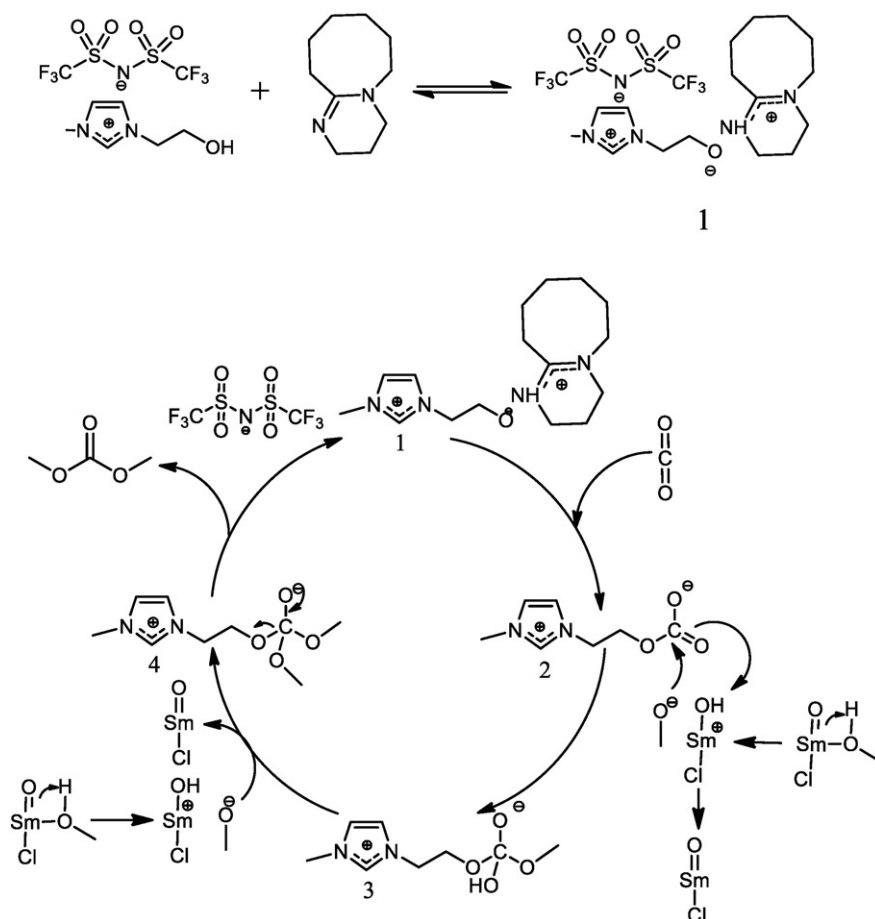
Methanol (25 ml, 0.625 mol) and [HEMIm][NTf₂] IL (4 g, 0.07 mol) with DBU (0.007 mol) and samarium oxychloride (SmOCl) (0.005 mol) were charged into the reactor. The reaction was carried out at 140 °C under continuous stirring at 700 rpm for 4 h. After completion of reaction, the reaction mixture was distilled to separate the IL. The DMC in liquid phase was analyzed by gas chromatography (GC-17A, Shimadzu Corporation) using capillary column (Stabilwax, 30-m-long, 0.53-mm inner diameter, and 1-μm film thickness) equipped with a flame ionization detector. The amount of the product was determined using the external standard method. Furthermore, DMC was identified by ¹H NMR, FTIR, and gas chromatography–mass spectrometry (GC–MS).

3. Results and discussion

3.1. Catalyst characterization

3.1.1. TGA of [EmimOH][NTf₂] IL

TGA is very important for estimating the stability of the IL. The NTf₂-containing room temperature ionic liquid has a wider liquid



Scheme 1. Predicted mechanism for synthesis of DMC in the presence of IL, DBU, and SmOCl.

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