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Review

Phosgene-free approaches to catalytic synthesis of diphenyl carbonate and its intermediates

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Abstract

Diphenyl carbonate (DPC) is considered as a substitution for phosgene to synthesize polycarbonate resins. Conventional production of DPC involves reactions of phosgene and phenol. However, the phosgene process has drawbacks such as environmental and safety problems associated with using highly toxic phosgene as the reagent, which results in the formation of chlorine salts, and copious amounts of methylene chloride as the solvent. For these reasons, environmentally friendly processes for DPC production without using phosgene have been proposed and developed in the past decades. So far, the most promising alternatives appear to be the transesterification of dimethyl carbonate (DMC) and phenol, the direct oxidative carbonylation of phenol, and transesterification of dialkyl oxalates and phenol. This paper attempts to review recent literature concerning process design and catalytic chemistry for these phosgene-free approaches. The advantages and disadvantages are discussed for each reaction. Strategies to overcome potential problems are provided. The perspectives to improve catalytic efficiency of phosgene-free process are proposed.

Keywords: Review; Catalysis; Polycarbonates; Phosgene-free; Environmental; Diphenyl carbonate; Dimethyl carbonate; Methyl phenyl carbonate; Carbonylation; Transesterification; Dimethyl oxalate; Diethyl oxalate; Diphenyl oxalate; Methyl phenyl oxalate; Decarbonylation; Heterogeneous; Homogeneous; Supported catalyst; Palladium; MoO_3; TiO_2

Contents

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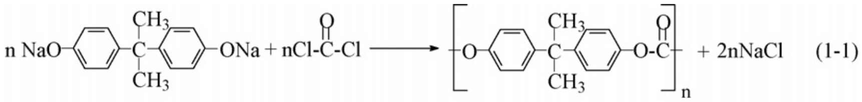
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Scheme 1. PC synthesis from interfacial polycondensation of bisphenol-A salt in an aqueous caustic solution and phosgene in an organic solution.

1. Introduction

Polycarbonates (PCs) are important engineering thermoplastics with excellent mechanical, optical, electrical, and heat resistance properties [1]. Annual market growth for aromatic PCs has been more than 10% from the late 1990s. Currently, the worldwide production capacity of PC is more than 1.5 million t/year, and the construction of new PC plants is very likely to continue [2,3]. Currently, the interfacial polycondensation of bisphenol A (BPA) with phosgene (Scheme 1) is the primary commercial method for PC synthesis [3,4]. Major drawbacks of the conventional phosgene process are environmental and safety problems involved with using copious amounts of methylene chloride as the solvent, which is 10 times the weight of the products, and highly toxic phosgene as the reagent. With increasing demands for safer and cleaner processes, the hazardous phosgene process has to be improved or essentially replaced by more environmentally friendly or compatible processes [5]. For example, the transesterification of diphenyl carbonate (DPC) with BPA (Scheme 2) shows promise as a phosgene-free route. As a matter of fact, GE (Cartagena, Spain), Bayer (Antwerp, Belgium), and Asahi Kasei (Taiwan) have introduced new non-phosgene-based manufacturing units using DPC as the carbonylation agent, which may lead to elimination of solvents and lowering fixed capital investment. In 2002, about 12% of polycarbonates were produced by phosgene-free technology. By 2007, this portion is expected to be greater than 20%. Because of the environmental and economic advantages of non-phosgene processes, DPC synthesis has received much attention as an alternative precursor to PC production.

Diphenyl carbonate has versatile chemical properties and has been used both as a phenylating agent and a methoxycarbonylating agent, which are very important in synthetic chemistry [3–6]. For example, DPC is used as an intermediate for the synthesis of low molecular weight aliphatic mono-isocynates starting from the corresponding ureas or allophenates [7]. Diphenyl carbonate can also be used to increase the viscosity of polycondensates such as polyamides and polyesters [8]. Dicarboxylic acids react with diphenyl carbonate to eliminate carbon dioxide and form diphenyl esters, which are the starting materials for the production of high molecular weight aromatic polyesters [9,10].

The industrial methods which are most commonly employed for the synthesis of diphenyl carbonate are based on the reaction of phosgene and phenol in the presence of bases [6,11,12] (Scheme 3). Again, the obvious disadvantages of the method are the use of phosgene as a raw material and the formation of stoichiometric amount of NaCl.

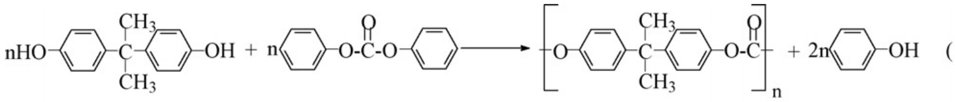
Therefore, considering the social and environmental effects of pollution, it is of the utmost importance to find a phosgene-free route for DPC synthesis. So far, several non-phosgene approaches for DPC production have been explored and developed [3,6]. Among them, the transesterification of dimethyl carbonate (DMC) and phenol [24–44,47,50–59], the oxidative carbonylation of phenol [60–89,91–115], and the transesterification of dialkyl oxalates [especially dimethyl oxalate (DMO)] and phenol [117–119,121–131,134–140,142–161] are the most attractive and promising alternatives to the phosgene route.

In spite of burgeoning number of explorations and applications, there is no detailed compilation of the literature on non-phosgene DPC synthesis. Therefore, in the present work, the reaction characteristics of the phosgene-free approaches are reviewed and advantages and disadvantages of each reaction are discussed based on the experimental results obtained by us and other investigators. Further, the catalytic chemistry of each reaction is compared regarding intrinsic catalytic properties under similar conditions.

2. DPC synthesis by transesterification of DMC and phenol

2.1. DMC synthesis from molecular oxygen, carbon monoxide, and methanol

DMC is achieving increasing importance in the chemical industry mainly for two aspects: first of all, its versatility as a reagent and a solvent; second, its green properties for human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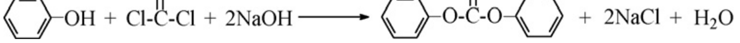
Scheme 2. PC synthesis from transesterification of BPA and DPC.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Scheme 3. DPC synthesis from the reaction of phosgene and phenol.