

Synthesis of cyclic carbonates from epoxides or olefins and CO₂ catalyzed by metal-organic frameworks and quaternary ammonium salts

Olga V. Zalomaeva^a, Nataliya V. Maksimchuk^a, Andrey M. Chibiryaev^b,
 Konstantin A. Kovalenko^c, Vladimir P. Fedin^c, Bair S. Balzhinimaev^{a*}

a. Boreskov Institute of Catalysis, pr. Akademika Lavrentieva, 5, Novosibirsk 630090, Russia

b. Vorozhtsov Novosibirsk Institute of Organic Chemistry, pr. Akademika Lavrentieva, 9, Novosibirsk, 630090, Russia

c. Nikolaev Institute of Inorganic Chemistry, pr. Akademika Lavrentieva, 3, Novosibirsk, 630090, Russia

[Manuscript received November 13, 2012; revised November 26, 2012]

Abstract

Catalytic properties of the metal-organic framework Cr-MIL-101 in solvent-free cycloaddition of CO₂ to epoxides to produce cyclic carbonates using tetrabutylammonium bromide as co-catalyst have been explored under mild reaction conditions (8 bar CO₂, 25 °C). Styrene and propylene carbonates were formed with high yields (95% and 82%, respectively). Catalytic performance of Cr-MIL-101 was compared with other MOFs: Fe-MIL-101, Zn-MOF-5 and HKUST-1. The catalytic properties of different quaternary ammonium bromides, Cr-MIL-101 as well as PW₁₂/Cr-MIL-101 composite material have been assessed in oxidative carboxylation of styrene in the presence of both *tert*-butyl hydroperoxide and H₂O₂ as oxidants at 8–100 bar CO₂ and 25–80 °C with selectivity to styrene carbonate up to 44% at 57% substrate conversion.

Key words

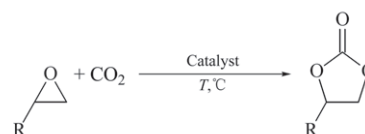
carbon dioxide; cyclic carbonates; cycloaddition; heterogeneous catalysis; metal-organic framework; oxidative carboxylation; quaternary ammonium salts

1. Introduction

Carbon dioxide is one of the major green-house gases, which is produced from chemical and energy supply industries, power plants and transportation sector. CO₂ is also an abundant, inexpensive, non-toxic and biorenewable C₁ resource. Nowadays, chemical transformation of CO₂ into valuable organic chemicals has attracted increasing attention from both environmental and resource utilization viewpoints. However, CO₂ molecule is thermodynamically stable and low reactive, so substantial energy input, proper catalysts and optimum reaction conditions are necessary for its chemical activation and further successful conversion to different commercial products [1,2].

Selective cycloaddition of CO₂ to epoxides as well as oxidative carboxylation of olefins are potentially significant approaches for both chemical utilization of CO₂ and production of cyclic organic carbonates. Cyclic carbonates provide an application as a raw material in the synthesis of polycarbonates and glycols as well as fuel additives, electrolyte solvents for lithium batteries, and substitutes for non-environmental or-

ganic solvents and toxic chemical reagents [3–5]. Most common methodology for the preparation of cyclic carbonates is based on the cycloaddition of CO₂ to the corresponding epoxides.



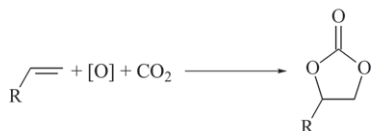
Currently, industry uses quaternary ammonium salts, e.g., tetraethylammonium bromide [6], or their solid forms [7] as catalysts for the synthesis of cyclic carbonates. However, these processes require high pressure of CO₂ (70–100 bar) and high reaction temperature (100–200 °C) that make them unfavorable from the viewpoints of energy consumption and safety. A lot of homogeneous and heterogeneous catalytic systems have been suggested for the synthesis of cyclic carbonates [8,9]. For homogeneous systems, catalysts are salen, porphyrin, phthalocyanine and other complexes of the main group and transition metals (Zn, Al, Cr, Co, Cu, Ni, Sn) [10–16], as well as quaternary ammonium salts [17], ionic

* Corresponding author. Tel: +7-383-3309770; Fax: +7-383-3308056; E-mail: balzh@catalysis.ru

This work was supported by the Russian Foundation for Basic Research (RFBR grant 12-03-31537).

liquids [18] and polyoxometalates [19]. Some of these complexes are effective at low pressure and temperature [11,12,14–16], but a complicated separation of the catalysts from the reaction product limits their application. Several solid catalysts have been explored for this reaction, e.g. metal oxides [20,21], immobilized complexes or ionic liquids [22–24] titanosilicates [25], and zeolites [26]. There are also few examples of the use of the metal-organic frameworks (MOFs), namely Zn-MOF-5 [27,28], Zn-ZIF-8 [29], Co-MOF-74 [30] and IRMOF-3 [31], in this reaction. In general, the majority of the reported catalytic systems requires high pressure and/or high temperature conditions. Therefore, the search for new catalysts and energy efficient processes remains to be a challenge.

Direct synthesis of cyclic carbonates from corresponding olefins and CO₂, so-called “oxidative carboxylation”, is more environmentally benign and an economical process because of the less expensive and easily available raw materials and avoidance of initial synthesis and separation of epoxides. Although the oxidative carboxylation of olefins has been known for over four decades [32], only a few catalytic systems have been reported so far [2]. Both homogeneous (rhodium salts) [33] and heterogeneous (metal oxides Nb₂O₅, MgO, Fe₂O₃, V₂O₅, etc.) [34] catalysts in combination with O₂ and CO₂ gave quite low (17%–20%) carbonate selectivity under harsh reaction conditions (120 °C, 5 bar O₂, 45 bar CO₂). The use of *tert*-butyl hydroperoxide (TBHP) as oxidant instead of O₂ and ionic liquids as catalysts increases carbonate selectivity up to 36%, but still requires high CO₂ pressure (20 bar) [35–37].



Metal-organic frameworks have attracted great attention of researchers due to the practical interest in their application in separations, gas storage and heterogeneous catalysts [38–41]. MOFs possess a unique ensemble of properties, such as high surface area, crystalline open structures, tunable pore size and functionality. Furthermore, MOFs are able to adsorb large amounts of gases, including CO₂ [42,43].

Until recently, a serious disadvantage of MOFs that limited their application in catalysis was low thermal and hydrolytic stability. Chromium terephthalate Cr-MIL-101 discovered by Férey and co-workers in 2005 is resistant to air, water, common solvents and has a fairly good thermal stability (up to 300 °C) [44]. This material has a rigid zeolite crystal structure consisting of quasi-spherical cages of two modes (2.9 and 3.4 nm). These features prompted us to investigate the catalytic potential of Cr-MIL-101 for the synthesis of cyclic carbonates via the cycloaddition of CO₂ to organic epoxides and oxidative carboxylation of olefins.

In the present work, we report the catalytic study on the synthesis of cyclic carbonates from epoxides and olefins. The cycloaddition of CO₂ to epoxides was performed in the presence of Cr-MIL-101 under mild solvent-free conditions,

which are attractive from both economic and environmental viewpoints. The catalytic properties of Cr-MIL-101 were compared with other typical MOFs such as Fe-MIL-101, Zn-MOF-5 and HKUST-1. The oxidative carboxylation of olefins was studied using quaternary ammonium salts as catalyst and TBHP or hydrogen peroxide as oxidant under both high and low pressure/temperature conditions.

2. Experimental

2.1. Catalysts and materials

Styrene oxide (SO) (97%), propylene oxide (PO) (99%), propylene carbonate (PC), TBHP (5.5 M solution in decane), tetrabutyl-, tetrahexyl- and tetraheptylammonium bromides (99%) were purchased from Aldrich. TBHP (70% aqueous solution) was purchased from Merck and urea hydrogen peroxide adduct was purchased from Fluka. Commercially available carbon dioxide with a purity of 98.8% was used without purification. The other reactants were obtained commercially and used as received.

The metal-organic framework Cr-MIL-101 with the formula of Cr₃F_{0.8}(NO₃)_{0.2}(H₂O)₂O[(O₂C)–C₆H₄–(CO₂)₃·*n*H₂O (*n*≈25) was synthesized following a procedure similar to that described by Férey et al. [44]. Activation of Cr-MIL-101 was carried out by drying under vacuum at 150 °C for 5 h and then at 180 °C for 2 h. The specific surface area and pore volume of Cr-MIL-101 determined by Brunauer-Emmett-Teller (BET) method were 3270 m²·g^{−1} and 1.47 cm³·g^{−1}, respectively. The chromium content was 23 wt%.

The other MOFs were synthesized according to the protocols reported earlier: Fe-MIL-101 [45], Zn-MOF-5 [46] and HKUST-1 [47]. PW₁₂/MIL-101 material was prepared by sorption of [PW₁₂O₄₀]^{3−} on Cr-MIL-101 from aqueous solution at room temperature according to Ref. [48].

2.2. General procedure for coupling reaction of epoxides and CO₂ under mild conditions

Epoxide (18 mmol), Cr-MIL-101 (50 mg, 0.2 mmol Cr) and tetrabutylammonium bromide (TBABr) (0.3–0.6 mmol) were loaded into a 100 mL high pressure stainless steel reactor. CO₂ was introduced into the autoclave and the pressure was adjusted to 8 bar. The mixture was stirred continuously while the pressure and temperature (25–80 °C) were kept constant during the reaction. After the reaction, the reactor was cooled in ice-water bath or liquid nitrogen (in the case of propylene oxide) and extra CO₂ was vented slowly. The reaction products were identified by GC-MS and ¹H nuclear magnetic resonance spectroscopy (NMR). A sample was taken from the reaction mixture, dissolved in CH₂Cl₂ and analyzed by GC after addition of internal standard (biphenyl) to determine the conversion of styrene oxide or propylene oxide and the yield of the corresponding carbonates.

Download English Version:

<https://daneshyari.com/en/article/63894>

Download Persian Version:

<https://daneshyari.com/article/63894>

[Daneshyari.com](https://daneshyari.com)