



Cyclic carbonates synthesis from epoxides and CO₂ over metal–organic framework Cr-MIL-101

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

^a Bokeskov Institute of Catalysis, 5, av. Acad. Lavrentiev, Novosibirsk 630090, Russia

^b Vorozhtsov Novosibirsk Institute of Organic Chemistry, 9, av. Acad. Lavrentiev, Novosibirsk 630090, Russia

^c Nikolaev Institute of Inorganic Chemistry, 3, av. Acad. Lavrentiev, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:

Received 2 August 2012

Revised 27 October 2012

Accepted 27 November 2012

Available online 4 January 2013

Keywords:

Carbon dioxide

Cyclic carbonates

Cycloaddition

MIL-101

Heterogeneous catalysis

Metal–organic framework

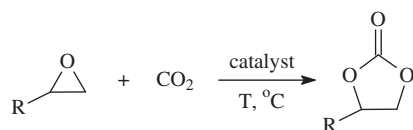
ABSTRACT

The catalytic performance of the metal–organic framework Cr-MIL-101 in solvent-free coupling of CO₂ and epoxides to produce cyclic carbonates has been explored at both high-pressure (100 atm CO₂) and low-pressure (8 atm CO₂) conditions in the temperature range of 25–120 °C. The presence of tetrabutylammonium bromide as co-catalyst was found to be crucial for the formation of the cyclic carbonates at mild reaction conditions (8 atm CO₂, 25 °C). The yield of the styrene carbonate attained 95% at 98% substrate conversion after 48 h. Cycloaddition of CO₂ to propylene oxide gave propylene carbonate with 82% yield at 91% conversion after 24 h. Heterogeneous nature of catalysis was proved by hot catalyst filtration test, indicating no leaching of active chromium species. However, a deterioration of the catalytic properties occurred after catalyst recycling due to pores blockage with the reaction products and gradual degradation of the MIL-101 structure.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

Carbon dioxide has received great attention as an abundant, cheap, non-toxic and renewable C₁ resource, and the development of the methods for its activation at mild conditions is an attractive research goal [1,2]. The selective cycloaddition of CO₂ to epoxides is a potentially significant approach for both chemical utilization of CO₂ and production of the cyclic carbonates, which finds a wide application as a raw material in the synthesis of polycarbonates and glycols as well as electrolyte solvents for lithium batteries, fuel additives, and substitutes for non-environmental organic solvents and toxic chemical reagents [3–5]. A common methodology for the preparation of the cyclic carbonates is based on a coupling reaction of the corresponding epoxides and CO₂.



Currently, industry uses quaternary ammonium salts, for example, tetraethylammonium bromide, as catalysts for the synthesis of the cyclic carbonates [6]. The recently developed Asahi Kasei process utilizes an anion exchange material with (CH₃)₄NCl groups as a heterogeneous catalyst for the production of ethylene carbonate, which is used as an intermediate in the synthesis of monoethylene glycol [7]. These processes require high pressure of CO₂ (70–100 atm) and high reaction temperature (100–200 °C). This makes them unfavorable from the points of view of energy consumption and safety. Recent reviews discuss numerous homogeneous and heterogeneous catalysts used for the synthesis of the cyclic carbonates [8–10]. Homogeneous catalysts include salen, porphyrin, phthalocyanine and other complexes of the main group and transition metals (Zn, Al, Cr, Co, Cu, Ni, Sn) [11–17], quaternary ammonium salts [18], ionic liquids [19], and polyoxometalates [20]. Some homogeneous complexes are effective at low pressure and temperature [12,13,15–17], but a complicated separation of the catalysts from the reaction product limits their application. Several heterogeneous catalysts have been explored for the cycloaddition of CO₂ to epoxides, such as metal oxides [21,22], immobilized complexes or ionic liquids [23–25], titanosilicates [26], and zeolites [27]. There are also few examples of the use of the metal–organic frameworks (MOFs), Zn-MOF-5 [28,29], Zn-ZIF-8 [30], Co-MOF-74 [31], and IRMOF-3 [32] in this reaction. The majority of the catalytic systems reported thus far for CO₂ cycloaddition requires

* Corresponding author. Fax: +7 383 3308056.

E-mail address: zalomaeva@catalysis.ru (O.V. Zalomaeva).

high-pressure and/or high-temperature conditions. Therefore, the search for new catalysts and energy efficient processes remains to be a challenge.

Chromium terephthalate MIL-101 discovered by Férey and co-workers in 2005 is a mesoporous metal–organic framework which possesses extremely high surface area and pore volume, is resistant to air, water, common solvents, and has a fairly good thermal stability (up to 300 °C) [33]. This material has a rigid zeotype crystal structure consisting of quasi-spherical cages of two modes (2.9 and 3.4 nm). Cr-MIL-101 was reported to catalyze effectively various types of reactions, including cyanosilylation of benzaldehyde, sulfoxidation of thioethers, and oxidation of hydrocarbons [34–38]. Furthermore, this MOF is able to adsorb large amounts of gases, including CO₂ [39,40]. These features prompted us to investigate the catalytic potential of MIL-101 for the synthesis of the cyclic carbonates via cycloaddition of CO₂ to the organic epoxides. In the present work, we report the results of the catalytic study of this reaction in the presence of MIL-101 under solvent-free conditions, which are attractive from both economic and environmental viewpoints. Both high-pressure and low-pressure conditions were explored. The optimization of the catalytic system to produce cyclic carbonates with maximal yields was performed. The possibility of the catalyst recovery and recycling was evaluated.

2. Experimental

2.1. Catalysts and materials

Styrene oxide (SO) (97%), propylene oxide (PO) (99%), cyclohexene oxide (98%), tetrabutyl- and tetrahexylammonium bromides (99%) were purchased from Aldrich, and propylene carbonate (PC) (99.5%) was purchased from Acros. Commercially available carbon dioxide with a purity of 98.8% was used without purification.

The metal–organic framework Cr-MIL-101 with the formula Cr₃F_{0.8}(NO₃)_{0.2}(H₂O)₂O[(O₂C)–C₆H₄–(CO₂)₃·nH₂O (n ~ 25) was synthesized following a procedure similar to that described by Férey et al. [33]. A mixture of 1.2 g (3 mmol) of Cr(NO₃)₃·9H₂O, 500 mg of terephthalic acid (H₂bdc, 3 mmol), and 0.6 ml of 5 M HF (3 mmol) in 15 ml H₂O was heated at 220 °C for 8 h in a Teflon-lined stainless steel bomb. The resulting green solid was passed through a coarse glass filter to remove the unreacted colorless crystals of H₂bdc and then filtered on the dense paper filter. The crude MIL-101 was purified by double treatment with *N,N*-dimethylformamide (DMF) at 60 °C for 3 h and then by triple treatment with ethanol at 70 °C for 2.5 h. Activation of 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 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.%.

2.2. General procedure for coupling reaction of epoxides and CO₂ at high pressure

A batch reactor was charged with styrene oxide (5 mmol) and catalyst (50 mg; 0.22 mmol Cr) and then pressurized with CO₂ up to 100 atm. All reactions were carried out at constant temperature of 70 °C. The mixer speed was 600 rpm in all experiments. After the reaction, the reactor was cooled to room temperature and CO₂ was released (~1.5 h) and then ethyl acetate was added into the reactor using a syringe pump. After washing the reactor's walls, the solution of the reaction mixture was dumped into a vessel and analyzed by gas chromatography–mass spectrometry (GC–MS) and gas chromatography (GC, see below details of the product analysis).

2.3. General procedure for coupling reaction of epoxides and CO₂ at mild conditions

Epoxide (18 mmol), Cr-MIL-101 (25–100 mg; 0.11–0.45 mmol Cr), and tetrabutylammonium bromide (TBABr) (0.15–0.6 mmol) were added into a 100-mL stainless steel autoclave reactor. CO₂ was introduced into the autoclave, and the pressure was adjusted to 8 atm. The mixture was stirred continuously while the pressure and temperature (25–120 °C) were kept constant during the reaction. After the reaction, the reactor was cooled in ice-water or liquid nitrogen (in the case of propylene oxide and cyclohexene 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. The conversion of cyclohexene oxide and the yield of cyclohexene carbonate were determined by ¹H NMR in CDCl₃ solution. Styrene carbonate (SC) was isolated from the reaction mixture by column chromatography on SiO₂ using a mixture of hexane and ethyl acetate (v/v 100:1) as eluent. The purity of the carbonate was confirmed by GC–MS and ¹H NMR spectroscopy. The isolated yield of SC was ca. 10% lower compared to the yield determined by GC.

2.4. Study on catalyst recycling behavior and stability

After catalytic run, the reaction mixture was diluted with CH₂Cl₂ and the catalyst was separated by filtration and washed with CH₂Cl₂ and acetone. Then, it was either activated under vacuum (treatment I) or additionally treated with DMF at 60 °C for 3 h, filtered off, washed, dried in air at room temperature (treatment II), and then reused with fresh Bu₄NBr added into the system. The catalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) technique, and N₂ adsorption measurements before and after several reuse procedures. The nature of catalysis (true heterogeneous versus homogeneous) was studied according to the methodology suggested by Sheldon et al. [41]. The content of chromium in the carbonate product was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Treatments of MIL-101 with PC were performed under the following reaction conditions: PC 2.5 mL (30 mmol), MIL-101 75 mg, TBABr 0.47 mmol (when added), P(CO₂) 8 atm, 25 °C, 48 h. Then, the catalyst was characterized by FT-IR spectroscopy, XRD, and N₂ adsorption measurements.

2.5. Instrumentation

The experiments at high pressure were performed in a high-temperature batch reactor Autoclave Engineers with Hastelloy C-276 alloy as the reactor's wall material. The autoclave was equipped with mechanical agitator MagneDrive[®] and two thermocouples. The experiments at low pressure were performed in a stainless steel autoclave reactor. GC analyses were performed using a modernized Tsvet-500 gas chromatograph equipped with a flame ionization detector and DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm). GC–MS analyses of organic products were carried out using a HP 5890/II/5971 system (carrier gas He, 30 m × 0.25 mm × 0.25 μm capillary column HP-5) or Agilent 6890/MSD 5973 system (carrier gas He, 30 m × 0.25 mm × 0.25 μm capillary column HP-5). ¹H NMR spectra of the reaction products were run on Bruker Avance III 500. An analyzer SORB-TOMETER-M was used for measuring nitrogen adsorption characteristics and textural properties (specific surface area and pore volume) within the partial pressure of gas-adsorbate from 0.05 to 0.25 (multi-point BET method). FT-IR spectra were recorded on a

Download English Version:

<https://daneshyari.com/en/article/61320>

Download Persian Version:

<https://daneshyari.com/article/61320>

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