Journal of Molecular Catalysis A: Chemical 398 (2015) 42–49

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Highly active and reusable ternary oxide catalyst for dialkyl carbonates synthesis

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ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form
12 November 2014
Accepted 22 November 2014
Available online 28 November 2014

Keywords:
Dialkyl carbonate
Dimethyl carbonate (DMC)
Transesterification of cyclic carbonate
Ternary oxide
Rare-earth modified hydrotalcite
Solid base catalyst

ABSTRACT

The application of ternary oxides, prepared through calcination of rare-earth modified Mg/Al-hydrotalcite (HT), as highly active, selective, and reusable solid catalysts for dialkyl carbonates synthesis by transesterification reaction is reported. Dimethyl carbonate, for example, was prepared by reacting ethylene carbonate with methanol in 100 mol% selectivity at a yield of 95 mol%. Among several rare-earth modified precursors, La (10 mol%)-HT showed the highest activity. This catalyst was active even at ambient conditions. Basicity of the catalyst played crucial role on its performance. The activity of these catalysts was superior to the hitherto known solid catalysts for this reaction.

1. Introduction

Dialkyl carbonates such as, dimethyl carbonate (DMC), diethyl carbonate (DEC), etc., are an interesting class of green chemical intermediates. Worldwide consumption of DMC has been increasing continually because of its applications in fuel technology, pharmaceuticals and electrochemical, and catalytic reactions [1–4]. It is a widely used organic solvent and green reagent for alkylation and carbonylation replacing toxic dimethyl sulphate (DMS) and phosgene, respectively [4]. DMC offers a strong perspective to several organic reactions and refining industry to match the green chemistry principles [5,6]. Phosgenation, the traditional method for DMC and other dialkyl carbonates production is unsafe. Although oxidative carbonylation was represented as a milestone for green DMC synthesis [7], it is associated with hazard. Environmental-friendly routes for dialkyl carbonates synthesis are the direct synthesis from CO_2 and alcohol and transesterification of cyclic carbonates with alcohol [8–10]. The yield of DMC in the former route is low because of the thermodynamic limitation. Transesterification of cyclic carbonates with methanol is more promising alternate to the traditional methods of dialkyl carbonates synthesis. This reaction is catalyzed by both acids and bases. However, base catalyst is more active than acid catalyst. Sankar et al. [11] reported 80 mol% DMC yield from transesterification of ethylene carbonate (EC) with methanol at ambient condition using alkali and alkaline earth tungstate catalyst. Later, the same group [12] reported CaO–ZnO-based catalysts with varying Ca/Ca + Zn ratio for the synthesis of DMC with yield up to 84% at ambient conditions both in batch and continuous processes. Watanabe and Tatsumi [13] reported 70% EC conversion and 58% DMC selectivity over Mg–Al-HTs. Amine-functionalized MCM-41 catalyst provided DMC yield of 44 mol% in a continuous transesterification of EC with methanol [14]. According to Zhao et al. [15] quaternary ammonium salt functionalized chitosan gave DMC yield of 54% with a propylene carbonate (PC) conversion of 71%. Binary zinc–yttrium oxides were also tried for this reaction obtaining a maximum of 55% EC conversion with 54% of DMC yield [16]. Polyvinylpyridine (PVP) was found to be a highly efficient homogeneous recyclable catalyst for the reaction of EC with methanol [17]. PVP acted as a base catalyst via lone pair of electrons present on the nitrogen atom of the pyridine ring; distillation or phase separation was used to isolate the catalyst from reaction mixture. Tatsumi et al. [18] reported study on K-TS-1 catalyst for this reaction with 57% of DMC yield. Most of the hitherto known homogeneous or heterogeneous catalyst systems suffer from low catalytic activity, high reaction temperature,

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http://dx.doi.org/10.1016/j.molcata.2014.11.022
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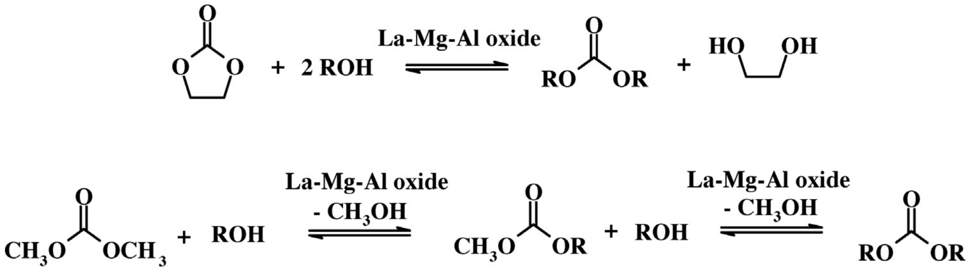

Scheme 1. Transesterification reaction for DMC.

and long reaction times. There is a need to develop more efficient catalyst for dialkyl carbonates synthesis. Hydrotalcites (HTs) are layered double-hydroxides (anionic clay) having a general formula $[M_{(1-x)}{}^{2+}\ M_x{}^{3+}(OH)_2]^{x+}(A^{n-}{}_{x/n})\cdot yH_2O$. Their structure resembles Brucite layered structure, in which a part of bivalent metal ions ($M^{2+} = Mg^{2+}$) is isomorphously substituted with trivalent metal ions (M^{3+}), resulting in excess positive charge which is balanced by anions ($A^{n-} = CO_3{}^{2-}$, $NO_3{}^{-}$, and Cl^-, etc.) present in the interlayers. HTs have gained increasing interest in recent years because of their potential application in various fields such as, CO_2 adsorbents, ion exchangers, fire retardants, base-catalyzed organic reactions, and convenient precursors of mixed oxides for various catalytic applications [19–22]. HTs are decomposed to yield homogeneous mixed oxides with strong Lewis base features. They are efficient solid base catalysts replacing homogenous bases like NaOH, KOH, etc., for transesterification reactions. Recently, we have reported the activity of calcined rare-earth modified HTs for DMC synthesis through transesterification of PC with methanol [23]. In that study, we modified Mg–Al-HT with rare-earth elements (La^{3+}, Ce^{3+}, Y^{3+}, Pr^{3+}, and Sm^{3+}). Different mole percentage of La containing Mg–Al-HT catalysts was also prepared by co-precipitation method, calcination of which yielded ternary lanthanum–magnesium–aluminum oxides. We, now, extend the applicability of those ternary oxides for transesterification of EC as well as DMC with different alcohols including methanol, ethanol, *n*-propanol, *n*-butanol, and benzyl alcohol producing various dialkyl carbonates along with ethylene glycol (EG) or methanol as co-product (Scheme 1). We have found that dialkyl carbonate synthesis starting with EC is more yielding and selective even at 40 °C than with PC and DMC. Catalytic activity correlates with the density of basic sites on the ternary oxide catalyst.

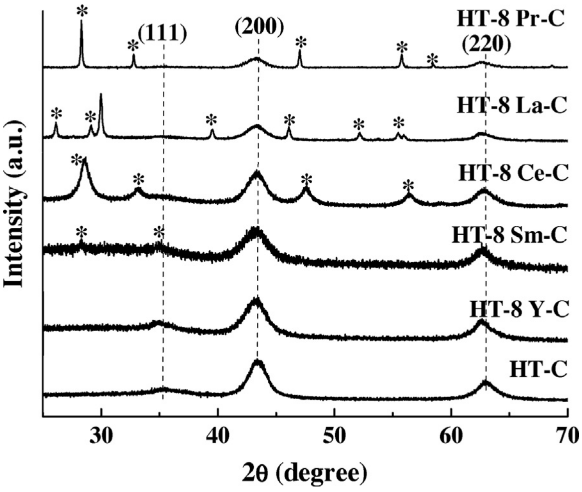

Fig. 1. Powder XRD patterns of calcined HT and rare-earth ion modified HT catalysts. Peaks marked by asterisk correspond to rare-earth oxide and oxide carbonate phases. Peaks corresponding to Mg(Al) oxide are indexed.

2. Experimental

2.1. Preparation of HTs and ternary oxides

Mg-Al-hydrotalcite (Mg:Al molar ratio = 2:1) and different rare-earth modified HTs were prepared by co-precipitation technique as reported by us earlier [23]. The materials obtained were labeled as HT-as-syn and HT-*X* M, respectively, where M is the rare-earth element and *X* stands for mole percentage of M. These materials were then calcined at 600 °C for 6 h. The mixed oxide, thus, obtained was designated as HT-C and HT-*X* M–C, respectively.

2.2. Characterization procedures

The composition of Mg, Al, and La ions in the ternary oxide samples was determined by inductively coupled plasma optical emission spectrometer (ICP-OES; Spectro Arcos) [23]. A known quantity of the catalyst (2–9 mg) was dissolved in a minimum amount of 2N HNO_3 and made up to the required volume (50 ml) before the ICP-OES analysis. X-ray diffraction (XRD) patterns of the powder samples were recorded on a Philips X'pert Pro diffractometer using Cu-Kα radiation and a proportional counter detector. Diffractographs were recorded in the 2θ range of 5–80° with a scan rate of 2°/min and step size of 0.02°. Specific surface area (S_{BET}) of the samples was determined by N_2 adsorption measurements at −196 °C using a NOVA 1200 Quantachrome equipment. FTIR spectra of the samples as KBr pellets were recorded on a Shimadzu 8201

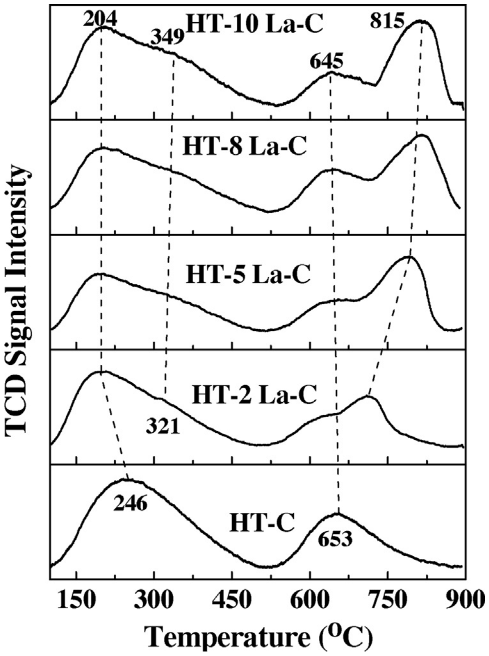

Fig. 2. CO_2-TPD profiles of calcined HT and rare-earth modified HT catalysts.