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Reusable Mg–Al hydrotalcites for the catalytic synthesis of diglycerol dicarbonate from diglycerol and dimethyl carbonate

Joseph A. Stewart, Bert M. Weckhuysen, Pieter C.A. Bruijnincx*

Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

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ABSTRACT

Diglycerol dicarbonate, which has been highlighted as a potential monomer for the production of non-isocyanate polyurethanes, has been synthesised using as-synthesised hydrotalcites of varying magnesium-to-aluminium ratio as catalyst materials. The hydrotalcite materials were aged for two different times, influencing their crystallite size. The catalytic carbonylation of diglycerol into diglycerol dicarbonate with dimethyl carbonate as "CO" source and solvent, ran to full conversion within 6 h, with complete selectivity, operating at relatively mild temperatures. Diglycerol monocarbonate was observed as a reaction intermediate in this conversion process. The increased basicity observed with increasing Mg/Al ratio led to higher activities. The catalysts can be easily recovered and re-used without any further activation treatment, whilst still displaying their high activity.

1. Introduction

Glycerol is considered an important renewable platform molecule for the synthesis of various bulk and specialty chemicals [1,2]. It is traditionally produced in large amounts by simple hydrolysis of triglycerides [3]. More recently, large volumes of glycerol are also being produced as a by-product of biodiesel production by trans-esterification, with about 110 kg of crude glycerol being produced per ton of biodiesel. This has led to a surplus of glycerol flooding the market, with traditional outlets such as pharmaceuticals, the food industry and solvents, not being able to make use of this excess. Even though the longer-term viability of biodiesel production from oils and fats is debateable, current production projections still forecast a growth in Europe of about 140 million metric tons between 2030 and 2050 [4]. Moreover, glycerol is expected to play a major role in future biorefinery systems. The effect of this new and growing glycerol source is that the readily available glycerol becomes inexpensive, with some projections suggesting the price could be as low as $0.11 per kg for crude glycerol solutions [5]. This in turn makes the development of new glycerol-based products very attractive and a number of technologies have indeed been developed recently for conversion of glycerol to value-added chemicals.

Examples include the conversion of glycerol into glyceric acid by oxidation [6–9], propylene glycol and 1,3-propanediol by hydrogenolysis [10–14] and acrolein by dehydration [15–19]. In recent years, extensive research has also been carried out investigating the production of glycerol carbonate (GC) from glycerol [20]. GC can be used in a number of ways; applications range from renewable solvents and beauty products to building eco-composites to charge carriers in lithium batteries. It has already been incorporated into a number of companies' portfolios due to its attractive physical properties and reactivity. The advantages of using GC include it being non-flammable, non-toxic and biodegradable as well as water-soluble. GC derivatives have also been highlighted for potential use as monomers for non-isocyanate polyurethanes (NIPUs) [21].

Glycerol itself can also be condensed to dimers and oligomers [22], for instance, by catalytic etherification with simple alkaline or alkaline earth-based bases [23]. These highly functional molecules can in turn be used as or converted into multifunctional building blocks, such as cyclic carbonates, for the production of various polymers. The possibility of producing polyurethanes, a class of polymer in high demand, via a phosgene-free route by utilising these cyclic carbonates derived from glycerol holds great potential, for example [24]. In fact, diglycerol dicarbonate has been highlighted as a very desirable building block for this process [21].

While various routes have been reported and are being used for the production of glycerol carbonate [25–27], no catalytic routes to diglycerol dicarbonate have been reported to date. Phosgene has previously been used for the production of GC from glycerol, but its

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* Corresponding author. Tel.: +31 302537400; fax: +31 302511027.
E-mail address: p.c.a.bruijnincx@uu.nl (P.C.A. Bruijnincx).

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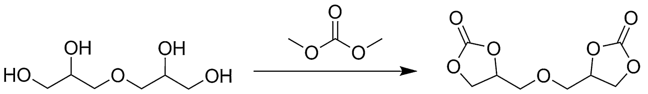
highly toxic nature has led to research into more environmentally friendly processes [28]. It has been shown that a number of different catalytic systems can be utilised for this process, as well as a range of "CO" sources. Direct synthesis from glycerol and CO_2 would appear to be a favourable route, as this would make the resulting glycerol carbonate 100% renewable; to date, glycerol conversions of only 35% have been achieved, however, which is attributed to the unfavourable thermodynamics of the reaction [29,30]. Alternatives to CO_2 have also widely been investigated. One such source is simply carbon monoxide for which good yields have been recorded in oxidative carbonylation reactions for a number of systems [31,32]. Transcarbonation, the carbonyl exchange reaction between alcohols and CO sources, of which phosgene is one example, holds a greater potential. Other than phosgene, two other classes of CO sources have been used in the synthesis of GC, namely dialkyl carbonates and cyclic carbonates such as ethylene and propylene carbonate, both of which have shown good conversion with a range of basic catalysts at relatively mild temperatures of around 100 °C [25,33,34].

Both homogeneous and heterogeneous catalyst systems have been reported for the formation of cyclic carbonates with various CO sources. These range from ionic liquids [35] to transition metal complexes [32] and supported metal catalysts [36] to simple (mixed)-metal oxides [37,38]. The mixed oxides have been shown to be particularly versatile and could be used with each of the reagents mentioned above. A number of alkaline earth metal oxides and mixed oxides of, e.g., Zr, Mg, Al and Ca, demonstrate high activity for the formation of GC. Of particular interest is the use of Mg–Al hydrotalcites, basic materials that are often used as precursor in the synthesis of heterogeneous mixed oxide bases. Hydrotalcites (HTs) are naturally occurring layered anionic clays with the general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}A^{n-}{}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal ions, and A^{n-} is the interlayer anion. The structure consists of positively charged brucite-like layers with the anions, e.g. hydroxide or carbonate anions, being intercalated between these layers compensating the positive charge caused by the introduction of the trivalent ions [39]. Upon heat treatment (i.e., when exposed to temperatures higher than 400 °C), these hydrotalcites lose their ordered structure and become mixed oxides. For hydrotalcites, basicity can be manipulated by varying the Mg–Al ratio. Increasing the number of M^{3+} species decreases the density of basic sites [40].

Climent et al. have demonstrated the use of various mixed oxides, including Mg–Al mixed oxides of varying Mg–Al ratio obtained by calcination of their hydrotalcite precursors, for the transesterification of ethylene carbonate with glycerol to form GC. They were able to achieve 85% conversion within 5 h with 96% selectivity at 50 °C with a Mg–Al mixed oxide of ratio 3:1 [25]. It was furthermore shown that the initial rates of the mixed oxide and a rehydrated HT were very similar, indicating that Brönsted basic sites are as active for the reaction. Interestingly, Takagaki and co-workers showed that as-synthesised, uncalcined hydrotalcites with Mg–Al ratios from 2 to 5 are indeed also active catalysts for the synthesis of GC from glycerol and DMC using DMF as a solvent. High turnover numbers were observed for the catalysts with a Mg–Al ratio of 3 to 5:1, with the catalyst with a nominal ratio of 5:1 (measured as 4.31) generating the highest GC yield of 75% at 100 °C. The authors indicated that the presence of hydromagnesite in the higher Mg–Al ratio catalysts, while being inactive itself, has a positive influence of the activity [26].

As evidenced by the examples listed above, to date only the catalytic conversion of glycerol to glycerol carbonate has been reported. However, for use in polymers, multifunctional monomers are needed making the conversion to diglycerol dicarbonate (DGDC) from diglycerol (DG) also of interest (Scheme 1). In this paper, we demonstrate that full conversion to DGDC can be achieved within 6 h using as-synthesised hydrotalcites and dimethyl carbonate as CO source as well as solvent. We will also show that these heterogeneous catalysts can easily be recovered and reused, whilst still maintaining their original selectivity.



Scheme 1. Reaction scheme of diglycerol to diglycerol dicarbonate utilising DMC as the CO source.

2. Experimental

2.1. Materials

Commercial hydrotalcites were purchased from Sasol, dimethyl carbonate from Merck (≥99%), anisole (99%), magnesium nitrate hexahydrate (99+%) and aluminium nitrate nonahydrate (99+%) from Acros and sodium carbonate decahydrate (99%) and sodium hydroxide (99%) were purchased from Sigma Aldrich. All materials were used as-received without further purification. Diglycerol (>80%) purchased from ABCR and shown by GC analysis to contain around 86% diglycerol and 5% glycerol, with the rest made up of higher oligomers.

2.2. Catalyst synthesis

Mg–Al hydrotalcites were prepared using an adapted literature coprecipitation method [26]. Mg–Al hydrotalcites of a nominal Mg/Al ratio of 2 and 5 were prepared by adding a solution of $Mg(NO_3)_2\cdot 6H_2O$ (50 or 20 mmol) and $Al(NO_3)_3\cdot 9H_2O$ (10 mmol) mixed in 100 mL deionised water dropwise to an alkaline solution of $Na_2CO_3\cdot 10H_2O$ (30 mmol) and NaOH (70 mmol) in 60 mL deionised water. This mixture was then stirred at 60 °C for 1 h, before increasing the temperature to 100 °C and stirring for a further 2 or 22 h as indicated. After the pre-determined time, the white precipitate was filtered and washed with copious amounts of distilled water. Samples were dried overnight at 120 °C before being sieved to a 212–425 μm sieve fraction.

Hydromagnesite ($Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$) was prepared by adding slowly a 1 M aqueous solution of $Mg(NO_3)_2\cdot 6H_2O$ (10 mmol) to a 1 M aqueous solution of $Na_2CO_3\cdot 10H_2O$ (6 mmol) and allowing it to stir at 45 °C for 24 h. The white precipitate was filtered, washed with distilled water and dried at 120 °C overnight [41].

2.3. Catalytic testing

Typical catalytic reactions were carried out in closed 8 mL glass vials. To diglycerol (2 mmol) was added dimethyl carbonate (20 mmol) and 0.1 g catalyst. The reaction was stirred at 130 °C for the desired reaction time, after which the reaction was cooled in a water bath and filtered using a 30 μm filter. The filtered catalyst was washed with acetone and the washing collected and added to the reaction mixture. The acetone was then removed *in vacuo* at 40 °C. 0.5 mL of anisole was added as internal standard for NMR measurements, which were made in DMSO-d6.

2.4. Characterisation and analysis

Thermal instability of the product, DGDC, prevented the use of gas chromatography as an analytical tool. Reactions were thus evaluated by NMR with the use of anisole as internal standard and compared to an authentic sample of DGDC.

NMR analysis: ^1H and ^{13}C NMR spectroscopic measurements were conducted at 25 °C on a Varian Oxford AS400 MHz