

An efficient and green transesterification of glycols into cyclic carbonates catalysed by KF/Ca–Mg–Al hydrotalcite

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An efficient, convenient, and environmentally friendly method was developed for the transesterification of glycols into cyclic carbonates catalysed by 5 wt% KF/Ca–Mg–Al hydrotalcite. Using as a model the reaction of glycerol with dimethyl carbonate (DMC), various parameters such as molar ratios, catalyst type and amount, reaction temperature and solvent were studied to optimise the reaction. Then, using the optimal conditions, the formation of the corresponding cyclic carbonates via transesterification of ethylene, propylene and styrene glycols with DMC using KF/Ca–Mg–Al hydrotalcite as solid base catalyst were achieved in good to high yields in short reaction times. The catalyst was conveniently separated and reused for ten cycles without appreciable decrease in its activity.

Keywords: 1,2-diol transesterification; dimethyl carbonate; alkene cyclic carbonates; heterogeneous catalyst; hydrotalcite

Biodiesel production has received much attention because of its potential as an alternative to fossil fuels as well as other renewable biofuels including bioethanol, biogas and bio-oil.^{1,2} During production of 1000 kg of fatty acid methyl ester (FAME) *via* transesterification of fatty acids with methanol, 100 kg of glycerol is inevitably formed as an undesired concomitant by-product. The majority of glycerol is currently consumed by combustion as a poor heat source.^{3–5} Therefore, it is of great industrial importance to use glycerol for the synthesis of more value-added chemicals. One of the useful transformations of glycerol is the synthesis of cyclic carbonates,^{6,7} which have been widely used as excellent solvents, precursors for polymeric materials, chemical intermediates for pharmaceuticals and many other biomedical applications.^{8,9} They are stable, polar compounds and for this reason they offer useful applications such as surfactant component, a non-volatile solvent for paint industries, coatings, polycarbonates and additives for detergents.¹⁰ In addition, the multi-electrophilic ability of glycerol carbonate was profitably utilised for thio-functionalised C-3 synthons.¹¹

Several methods have been described for the synthesis of this versatile molecule, including reaction of glycerol with the hazardous phosgene or carbon monoxide and oxygen at a high pressure in the presence of metallic catalysts.⁹ Attempts have also been made to produce glycerol carbonate directly from glycerol and CO₂ under supercritical conditions employing zeolites¹² or Sn catalysts,¹³ but difficult reaction conditions were required, and low yields were obtained. Glycerol carbonate may be industrially obtained from glycerol and ethylene carbonate or dialkyl carbonates by transesterification.¹⁴ Starting from ethylene carbonate, ethylene glycol is obtained as by-product which makes difficult the separation of products because of its high boiling point. One alternative is the use of dimethyl carbonate as carbonate source which can be manufactured by environmentally safe industrial methods and potentially from CO₂ and renewable sources.¹⁵ The base catalysed reaction has been carried out using homogeneous or heterogeneous base catalysts such as imidazolium-2-carboxylate,¹⁶ CaO,¹⁷ Mg/Al hydrotalcite¹⁸ or hydrotalcite-hydromagnesite.¹⁹ Though these catalytic systems can catalyse the synthesis of glycerol carbonate in moderate to good yields, some drawbacks remain, such as tedious workup, the use of expensive reagents, and poor

recyclability. Moreover, generally the product was restricted to the glycerol derivative. Consequently, there is scope for further research towards a simple procedure, employing more effective, reusable and inexpensive heterogeneous catalyst and expansion of substrate for the synthesis of a variety of cyclic carbonates.

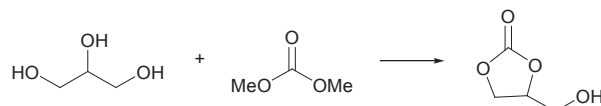
KF-loaded catalysts have been found to be very active in various base-catalysed organic transformations.^{20–23} Xu and Liu²⁴ recently reported that KF supported on mixed oxide efficiently catalysed biodiesel synthesis. In our previous work, KF/Ca–Mg–Al hydrotalcite has been developed for catalysing the transesterification reaction of vegetable oil with methanol and it exhibited high catalytic activity.²⁵ Therefore, we envisioned that KF/Ca–Mg–Al hydrotalcite could render a clear and efficient catalyst for transesterification of glycerol into glycerol carbonate. Furthermore, the substrate scope of the KF/Ca–Mg–Al hydrotalcite catalyst was also extended to use the different glycols including glycerol, propylene glycol, ethylene glycol and styrene glycol to obtain the corresponding cyclic carbonate from transesterification with DMC. It is an inexpensive and non-hazardous solid base catalyst which can easily be handled and removed from the reaction mixtures by simple filtration.

Results and discussion

To evaluate the catalytic performance of KF/Ca–Mg–Al hydrotalcite catalyst in the transesterification reaction, a series of reactions of glycerol and DMC under several sets of conditions were carried out (Table 1). Initially a series of catalysts was investigated. Note that this single-pot reaction at 80 °C in the presence of these catalysts does not lead to any side products. It showed that the transesterification reaction catalysed by the catalyst KF/Ca–Mg–Al hydrotalcite gave the highest yield in the shortest time (entry 6). Ca–Mg–Al hydrotalcite, lacking KF, resulted in a low yield of glycerol carbonate (entry 3), which means that the presence of KF was essential.

We then examined the influence of solvent using 5% (w/w) KF/Ca–Mg–Al hydrotalcite as the catalyst at 80 °C. Five reaction media were compared and the results are listed in Table 1. It was found that almost no product was obtained in toluene and THF (entries 7 and 10). When DMF and MeCN were used as solvent, the yields were 88 and 78%, respectively. In comparison, the reaction in the absence of solvent gave the best result (99% yield, entry 6). By decreasing the temperature to 60 °C, the ratio of DMC to glycerol and the catalyst amount, the yield of glycerol carbonate was conspicuously decreased (entries 11–13).

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Table 1 Optimisation of the transesterification of glycerol with dimethyl carbonate (DMC) using various catalysts and various solvents for different times^a

Entry	Catalyst	Catalyst amount/wt%	Molar ratio DMC/glycerol	Solvent	T/°C	t/h	Glycerol carbonate yield/% ^b
1	–	–	3	–	80	3	Trace
2	KF	5	3	–	80	1	91
3	Ca–Mg–Al HT	5	3	–	80	3	45
4	KF/Mg–Al HT	5	3	–	80	3	71
5	KF/Ca–Al HT	5	3	–	80	1	93
6	KF/Ca–Mg–Al HT	5	3	–	80	0.5	99
7	KF/Ca–Mg–Al HT	5	3	PhMe	Reflux	3	Trace
8	KF/Ca–Mg–Al HT	5	3	DMF	110	3	88
9	KF/Ca–Mg–Al HT	5	3	MeCN	Reflux	3	78
10	KF/Ca–Mg–Al HT	5	3	THF	Reflux	3	Trace
11	KF/Ca–Mg–Al HT	3	3	–	80	3	73
12	KF/Ca–Mg–Al HT	5	1	–	80	3	79
13	KF/Ca–Mg–Al HT	5	3	–	60	3	61

^aReaction conditions: glycerol (2 mmol) and dimethyl carbonate (6 or 2 mmol) were heated alone or in a solvent for various times in the presence of a catalyst (3 or 5 wt%).

^bBy quantitative GC analysis.

To meet economical interest and the principles of clean synthesis, the recycling of the catalyst was studied. KF/Ca–Mg–Al hydrotalcite was repeatedly used for the glycerol transesterification reaction. The catalyst was collected by filtering the mixture after reaction and directly used in a new reaction cycle without any treatment. Glycerol and DMC were added in similar amounts for the initial reaction. The activity of KF/Ca–Mg–Al hydrotalcite catalyst was found to remain almost unchanged (approx. 97%) even after ten cycles. Figure 1 which shows SEM images of KF/Ca–Mg–Al hydrotalcite (before reaction and after the 10th reaction cycle) reveals that the initial catalyst has irregular particles on the surface (Fig. 1a), which seemed to be desirable for the catalytic application. After the tenth cycle, however, particles were much more uniform in its crystallites (Fig. 1b). This shows that the reaction appears not to be sensitive to the structure of the catalyst.

To further elucidate the applicability of the KF/Ca–Mg–Al hydrotalcite catalyst, the transesterifications of ethylene glycol, propylene glycol and styrene glycol with DMC under the optimal conditions were carried out. As Table 2 shows, the catalyst gave good to excellent carbonate yields in the range 76–98%.

Experimental

Melting points were obtained with a Shimadzu DSC-50 thermal analyser. NMR spectra were obtained on a Bruker RX-500 Advance spectrometer (¹H NMR at 500 Hz, ¹³C NMR at 125 Hz) in CDCl₃ or DMSO-*d*₆ using tetramethylsilane as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. Mass spectra were recorded on a Saturn 2000 GC/MS instrument. SEM analyses were carried out using a FEI Sirion 200. Commercially available reagents were used without further purification.

Preparation of the catalyst

The KF/Ca–Mg–Al hydrotalcite solid base catalyst was prepared by the procedure described in our previous work.²⁵ In a typical synthetic run, solution A (200 mL) contained Ca(NO₃)₂·4H₂O (26.6 g, 112.5 mmol), Mg(NO₃)₂·6H₂O (28.8 g, 112.5 mmol) and Al(NO₃)₃·9H₂O (28.1 g, 75 mmol), where Ca:Mg:Al=1.5:1.5:1, at room temperature. Solution B composed of Na₂CO₃ (21.2 g, 200 mmol) and NaOH (16 g, 400 mmol). Both two solutions were synchronously dropped into water (100 mL) at 65 °C at pH 9–10 under vigorous stirring. After ageing for 72 h at 65 °C, the white solid obtained was filtered off and washed with excess water to remove sodium ions. The solid was dried at 100 °C overnight and calcined at 450 °C in static air for 5 h.

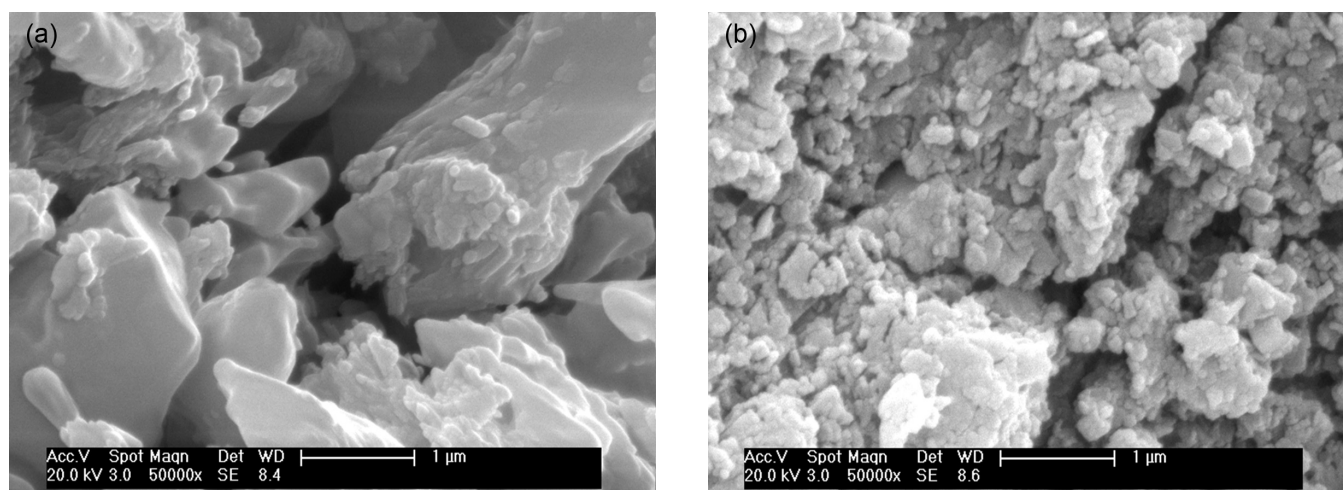


Fig. 1 SEM images of (a) KF/Ca–Mg–Al HT before and (b) after use in the catalytic reaction for 10 runs.

Table 2 Catalysed transesterification of various glycols with dimethyl carbonate (DMC)^a

Substrates	Products	Yield/% ^b
Ethylene glycol	Ethylene carbonate	98
Propylene glycol	Propylene carbonate	76
Glycerol	Glycerol carbonate	99
Styrene glycol	Styrene carbonate	91

^aReaction conditions: KF/Ca–Mg–Al HT (5 wt%), substrate (2.0 mmol), DMC (6 mmol), 80 °C, 0.5 h.

^bBy quantitative GC analysis.

KF/Ca–Mg–Al hydrotalcite was prepared by grinding the mixture of calcined powder and $\text{KF}\cdot 2\text{H}_2\text{O}$ with the mass ratio of 1:1 while dropping some water. Then the paste was dried at 65 °C overnight and further calcined in air at 550 °C for 5 h to yield KF/Ca–Mg–Al hydrotalcite.

Catalysed transesterification

Glycerol (0.184 g, 2 mmol), dimethyl carbonate (0.54 g, 6 mmol) and 5 wt% KF/Ca–Mg–Al hydrotalcite were added to a 25 mL flask equipped with a magnetic stirrer, condenser and thermometer. The reaction was carried out at 80 °C for 0.5 h with vigorous stirring. The reaction progress was monitored by GC analysis. After completion of the reaction, the solution was filtered. The filtrate was evaporated under reduced pressure, and finally the crude glycerol carbonate was obtained. The catalyst was reused for the next run.

In order to determine the isolated yields of cyclic carbonates, the residue was purified with silica gel column chromatography (AcOEt). All products were identified by comparing their melting points, ¹H NMR and ¹³C NMR spectra and MS with those of standard samples.

Glycerol carbonate: Oil; ¹H NMR ($\text{DMSO}-d_6$) δ 3.47–3.50 (m, 1H, CH₂), 3.62–3.67 (m, 1H, CH₂), 4.28 (d, d, $J=5.9, 8.4$ Hz, 1H, CH₂), 4.48 (t, $J=8.4$ Hz, 1H, CH₂), 4.73–4.81 (m, 1H, CH), 5.26 (t, $J=5.7$ Hz, 1H, OH); ¹³C NMR ($\text{DMSO}-d_6$) δ 61.7, 66.8, 77.1, 156.1; MS m/z : 118 (M^+).

Ethylene carbonate: M.p. 35–37 °C (ether) (lit.²⁶ 36–37 °C); ¹H NMR (CDCl_3) δ 4.51 (s, 4H, CH₂); ¹³C NMR (CDCl_3) δ 65.5, 156.4; MS m/z : 88 (M^+).

Propylene carbonate: Oil; ¹H NMR (CDCl_3) δ 1.53 (d, $J=6.2$ Hz, 3H, CH₃), 4.05 (d, d, $J=8.4, 8.4$ Hz, 1H, CH₂), 4.51 (d, d, $J=8.4, 8.4$ Hz, 1H, CH₂); ¹³C NMR (CDCl_3) δ 18.7, 71.5, 73.5, 154.7; MS m/z : 102 (M^+).

Styrene carbonate: M.p. 52–54.0 °C (EtOH) (lit.²⁷ 53–54 °C); ¹H NMR (CDCl_3) δ 4.37 (t, $J=8.2$ Hz, 1H, CH₂), 4.85 (t, $J=8.2$ Hz, 1H, CH₂), 5.71 (t, $J=8.2$ Hz, 1H, CH), 7.32–7.46 (m, 5H, CH); ¹³C NMR (CDCl_3) δ 72.1, 77.5, 126.8, 129.3, 129.8, 134.7, 155.6; MS m/z : 164 (M^+).

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