Synthesis of glycerol carbonate from glycerol and dialkyl carbonates using hydrotalcite as a reusable heterogeneous base catalyst†

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An uncalcined Mg–Al hydrotalcite catalyst involving hydromagnesite with a high surface area acted as a highly active base catalyst for glycerol carbonate synthesis from glycerol and dialkyl carbonates under moderate reaction conditions.

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] The biodiesel production capacity has increased annually at tremendous speed.[3] Production in 2008 in the European Union is estimated to be 7.8 millions of tons, 4 times larger than that in 2004.[4] During production of three moles of fatty acid methyl ester (FAME), one mole of glycerol is inevitably formed as an undesired concomitant product through transesterification of fatty acids with methanol. In other words, around 100 kg of glycerol is produced for every 1000 kg of biodiesel. This glycerol should be efficiently utilized to make valuable chemicals whereas the majority of glycerol is currently consumed by combustion as a poor heat source.[3] Glycerol can be converted into several important chemicals including acrolein by acid-catalysis,[5] propylene glycol and 1,3-propanediol by hydrogenolysis[6] and glyceric acid by oxidation.[7] Glycerol carbonate is one of the most attractive derivatives of glycerol.[2,3] It can be used as an elastomer, surfactant, adhesive, ink, paint, lubricant and electrolyte. It is also an important intermediate of polymers such as polycarbonate, polyester, polyurethane, and polyamide.

Glycerol carbonate was traditionally synthesized from glycerol with phosgene, which is, however, a highly toxic process.[8] Transesterification of glycerol with carbonates such as dialkyl carbonate and ethylene carbonate is an alternative way to produce glycerol carbonate under mild conditions. This base-catalyzed reaction has been carried out using homogeneous base catalysts such as Na_2CO_3 and NaOH.[9] From the viewpoint of green and sustainable chemistry, these homogeneous base catalysts should be replaced by heterogeneous ones because of some of their advantages including easy separation, non-toxicity, and reusability.[10] Although an attractive reaction has been reported, which is the direct formation from glycerol with CO_2 in the presence of an Sn-based catalyst,[11] some drawbacks remain, such as operational safety under high pressure and a considerably low yield of the product.

Herein, we have demonstrated glycerol carbonate synthesis from glycerol and dimethyl carbonate using a heterogeneous base catalyst, hydrotalcite, under mild reaction conditions. Hydrotalcite is a layered anionic clay denoted as $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}A^{n-}{}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal ions, and A^{n-} is the interlayer anion. Anionic species such as carbonate and hydroxide are located due to the charge compensation of the positively charged brucite layer. Mg–Al hydrotalcite, *i.e.* $Mg_6Al_2(OH)_{16}CO_3\cdot nH_2O$, is generally used as an active solid base catalyst for several reactions[12] including aldol condensation, the Knoevenagel reaction, epoxidation and transesterification.[13] Climent *et al.* recently reported that calcined hydrotalcite and mixed oxides efficiently catalyze glycerol carbonate synthesis from glycerol with ethylene carbonate or urea.[14]

Mg–Al hydrotalcites (Mg/Al = 2–5) were prepared by a conventional coprecipitation method. $Mg(NO_3)_2\cdot 6H_2O$ (20–50 mmol) and $Al(NO_3)_3\cdot 6H_2O$ (10 mmol) were dissolved in water (100 mL). The aqueous solution containing Mg and Al ions was added into an alkaline solution composed of $Na_2CO_3\cdot 10H_2O$ (30 mmol), NaOH (70 mmol) and water (60 mL) using a peristaltic pump at a speed of 1 mL min^{-1} at room temperature. After aging for an adequate time (0–18 h) at 338 K, the white-coloured solid was filtered off and washed with excess water (2 L) to remove sodium ions.[15] The obtained solid was dried at 373 K in an oven overnight.

The XRD patterns for samples aged for 18 h indicate all samples possess a typical hydrotalcite structure (see ESI† Figure S1). No impurity was observed for samples with a Mg/Al ratio of 2–4. The sample with a Mg/Al ratio of 5, however, has additional peaks attributed to hydromagnesite ($Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$).[16] Figure S1 also includes the XRD pattern for hydromagnesite, which was prepared in a similar manner to hydrotalcite synthesis.[16]

Mg/Al ratios of prepared samples were estimated by XPS analysis, indicating that the compositions of Mg and Al between Mg/Al ratios of 2–4 are close to those of initial ratios of these nitrates during synthesis as shown in Table 1. On the other hand, the sample prepared by a Mg/Al ratio of 5 did not match the original composition, and the ratio remained at 4.3. These results indicate that the hydrotalcite structure can be formed at Mg/Al ratios below 4, and the excess Mg ions are precipitated as another hydroxide, such as hydromagnesite under the preparation conditions.

The results of glycerol carbonate synthesis from glycerol and dimethyl carbonate through transesterification using prepared Mg–Al hydrotalcites are also listed in Table 1 (see ESI experimental†). On going from a Mg/Al ratio of 2 to 4, the

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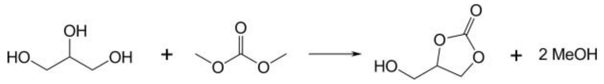
Table 1 Transesterification of glycerol and dimethyl carbonate using Mg–Al hydrotalcite[a]



	Mg/Al ratio				
	Prepared	Measured[b]	Glycerol carbonate yield/%	Base amount[c]/mmol g^{-1}	TON
Hydrotalcite	2	2.06	12	0.25	9.6
	3	3.04	21	0.19	22.1
	4	3.83	27	0.24	22.5
	5	4.31	75	0.64	23.4
Hydromagnesite	—	—	4	N. D.[d]	—

[a] *Reaction conditions*: Glycerol (2 mmol), dimethyl carbonate (10 mmol), DMF (5 mL), catalyst (0.1 g), 373 K, 1 h. [b] Determined by XPS. [c] Determined by addition of benzoic acid. [d] Not determined.

yield gradually increased from 12 to 27%. A significant increase of the yield was observed for samples between Mg/Al = 4 and 5. The yield was 75% at 373 K for 1 h for the sample with a Mg/Al ratio of 5. It should be noted that hydromagnesite itself exhibited poor activity (yield: 4%), indicating that the high activity for the sample of Mg/Al = 5 was attributed to hydrotalcite structure. The base amount estimated by the titration using benzoic acid[17] indicated that samples of low Mg/Al ratios (2–4) have a small amount of base sites whereas the sample with a Mg/Al ratio of 5 has a large amount of base sites (0.64 mmol g^{-1}). Turnover number based on the base amount and glycerol carbonate yield revealed that the catalytic activity was almost the same for the samples with Mg/Al ratios of 3–5, indicating that the strength of catalytically active sites of hydrotalcites was the same for all samples. The Mg/Al ratio affects the base amount of hydrotalcite, and a considerable amount of base sites was created at the samples of Mg/Al = 5 where the hydromagnesite phase was simultaneously formed.

The formation of hydromagnesite at samples of Mg/Al = 5 can be controlled by aging time at 338 K before drying during catalyst preparation. The XRD patterns for samples of Mg/Al = 5 with various aging time are shown in Fig. 1. As a comparison, those for samples of Mg/Al = 2 are also shown in the figure. For samples of Mg/Al = 2 (Fig. 1 (a)), the hydrotalcite structure remains unchanged through aging, and the peak intensity ascribed to hydrotalcite increased with increasing aging time. In contrast, a significant difference was observed at samples of Mg/Al = 5. After 2 h aging, samples begin to contain hydromagnesite along with hydrotalcite. Peak intensity for hydromagnesite increased with increasing aging time, resulting in the clear observation for 18 h aging.

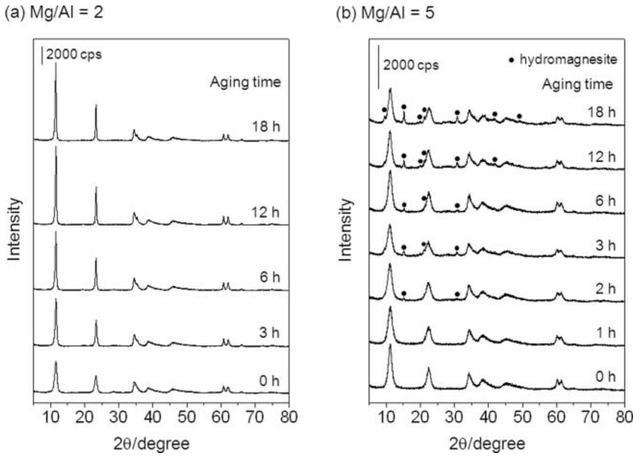


Fig. 1 XRD patterns for Mg–Al oxide samples with Mg/Al ratios of (a) 2 and (b) 5 prepared by aging at 338 K for 0–18 h.

The glycerol carbonate yield for transesterification and surface area of hydrotalcite of Mg/Al = 2 and 5 against aging time are shown in Fig. 2. The carbonate yield decreased with increasing aging time along with surface area for Mg/Al = 2

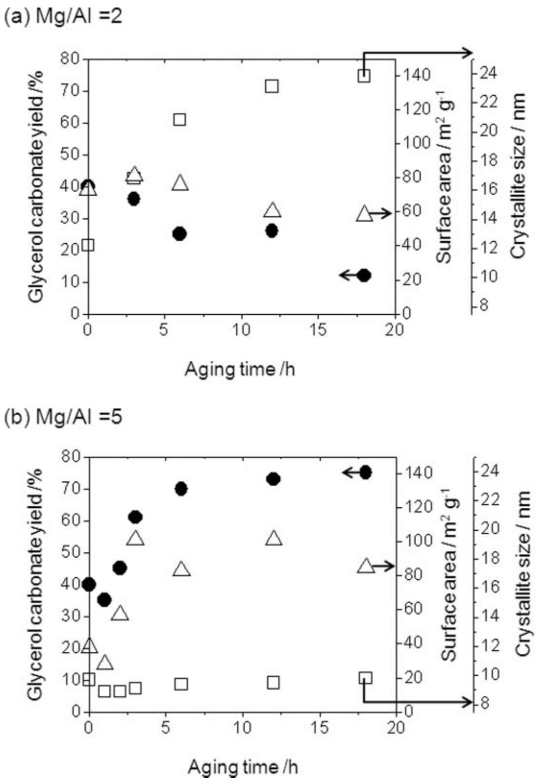


Fig. 2 Glycerol carbonate yield (filled circle) for transesterification and surface area (open triangle) of hydrotalcite *via* aging time during catalyst preparation. (a) Mg/Al = 2 and (b) Mg/Al = 5. Crystallite size (open square). *Reaction conditions*: Glycerol (2 mmol), dimethyl carbonate (10 mmol), DMF (5 mL), catalyst (0.1 g), 373 K, 1 h.

hydrotalcite. The average crystallite size, which was calculated by using Scherrer's equation on the (003) peak of XRD, is also included in the Figure. The crystallite sizes for samples of Mg/Al = 2 significantly increased with increasing aging time from 12.2 to 23.8 nm, leading to a decrease in activity for transesterification.

In contrast to the samples of Mg/Al = 2, both of the catalytic activity and surface areas of the samples of Mg/Al = 5 drastically increased with increasing aging time. The carbonate yield and the surface areas were linearly correlated.

Considering that hydromagnesite appeared during aging and it showed no activity, the occurrence of hydromagnesite should increase the surface areas of samples. The crystallite sizes for hydrotalcites of Mg/Al = 5 were from 8.9 nm to 9.8 nm, and base amounts remained unchanged between 0.63 to 0.65 mmol g^{-1}. The presence of hydromagnesite preserved the small size of hydrotalcite and increase of surface areas, resulting in high catalytic activity.

During aging Mg ions inside the hydrotalcite structure were considered to be partially dissolved into the solution. Some dissolved Mg ions seem to be converted into hydromagnesite through a dissolution-recrystallization process because Mg ions in the solution were in excess to form the hydrotalcite structure. Hydromagnesite has a relatively high surface area (60 m^2 g^{-1}), and therefore the resulting composite of hydrotalcite and hydromagnesite possesses not only basicity but also a high surface area. One possible explanation for the high yield of the product is a contribution of hydromagnesite to promote the activity of hydrotalcite. The prepared highly active HT may be a nanocomposite of hydrotalcite and hydromagnesite.

Although hydromagnesite hardly produced glycerol carbonate (4%), hydromagnesite itself could adsorb glycerol because of its apparent glycerol conversion of 19%. It is suggested that the adsorption of glycerol on hydromagnesite makes it easy to react with active base sites of hydrotalcite, *e.g.* the edge site.

The catalytic activity of prepared hydrotalcite (Mg/Al = 5) containing hydromagnesite was compared with conventional heterogeneous and homogeneous base catalysts. Table 2 lists the glycerol carbonate yield for transesterification using hydrotalcite, CaO and MgO with and without calcination. The use of $NaHCO_3$ or NaOH afforded 100% yield of glycerol carbonate under the reaction conditions. It seems that the equilibrium is exceedingly positioned to glycerol carbonate formation. As recently reported by Ochoa-Gómez *et al.*,[18] CaO calcined at high temperature exhibited high activity for the reaction whereas the uncalcined sample showed moderate activity which is lower than uncalcined hydrotalcite. MgO and $Mg(OH)_2$ showed low yields. In contrast, the activity of hydrotalcite decreased with increasing calcination temperature. The sample calcined at 673 K gave poor activity. The basicity of calcined hydrotalcite at 673 K was estimated to be 1.00 mmol g^{-1}, higher than that of the uncalcined one (0.64 mmol g^{-1}). The turnover number of the calcined sample is therefore 2.0 whereas that of the uncalcined one is 23.4. These results suggest that the active species of hydrotalcite are attributed to moderately strong hydrogen carbonate ions (HCO_3^-). The uncalcined hydrotalcite exhibited the highest activity among the solid bases tested. The yield of glycerol carbonate reached 99% for 2 h. The base amounts of CaO (calcined at 1173 K) and MgO determined by titration were 0.60 and 0.33 mmol g^{-1}, respectively. The turnover numbers are estimated to be 22.0 and 6.1 for CaO and MgO, respectively. The value for CaO is comparable to that of uncalcined hydrotalcite (23.4). The HT catalyst could be reused at least 3 times while keeping its high activity.[19] On the other hand, calcined CaO has the serious drawback of unrecyclability for further reuse.[18] The uncalcined hydrotalcite could produce glycerol carbonate in other polar aprotic solvents including *N*,*N*-dimethylacetamide, dimethyl sulfoxide and acetonitrile (see ESI Table S1†). Furthermore the catalyst could be used without solvent, resulting in a high yield (82%). In addition, an excellent result was obtained in the scale-up conditions; the glycerol carbonate yield was 98% from 100 mmol (9.2 g) of glycerol using 1.0 g of the hydrotalcite without solvent. The catalyst also exhibited high activity for glycerol carbonate formation from diethyl carbonate (see ESI Table S2†).

In summary, an uncalcined hydrotalcite catalyst with hydromagnesite was found to be an efficient solid base catalyst for glycerol carbonate formation from glycerol with dialkyl carbonates under mild reaction conditions. The high performance of the catalyst is ascribed to the small size of crystalline hydrotalcite with high surface areas in combination with hydromagnesite.

Table 2 Transesterification of glycerol and dimethyl carbonate using heterogeneous and homogeneous base catalysts[a]

Catalyst	Calcination *T*/K	Glycerol carbonate yield/%
HT (Mg/Al = 5)[b]	None	75, 99, [c]84, [d]82, [e]98[f]
	473	34
	523	10
	673	10
CaO[g]	None	43
	673	50
	1173	66
MgO[h]	None	10
	673	9
$Mg(OH)_2$[h]	None	10
γ-Al_2O_3	None	0
$NaHCO_3$[i]	—	100
NaOH[i]	—	100
Blank	—	0

[a] *Reaction conditions*: Glycerol (2 mmol), dimethyl carbonate (10 mmol), DMF (5 mL), catalyst (0.1 g), 373 K, 1 h. [b] Hydrotalcite. Aging time; 18 h. [c] 2 h. [d] 3rd use. Before the further reuse, the sample was washed with DMF (20 mL), water (60 mL) and acetone (60 mL). [e] Without solvent, 3 h. [f] Glycerol (100 mmol), dimethyl carbonate (500 mmol), catalyst (1.0 g), 373 K, 9 h. [g] Wako Pure Chemicals. [h] Kanto Chemical. [i] 0.1 mmol

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19 An apparent increase of yield (75 to 84%) seems to be due to the residue of glycerol during the recycle test. After the reaction, the catalyst was filtered off, and toluene solution containing phenolphthalein (pK_{BH+} 8.0–9.6) was added to the transparent filtrate, resulting in no change of color.