Electronic Supplementary Information for

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

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Experimental

Materials:

$Mg(NO_3)_2 \bullet 6H_2O$ (99 %), $Al(NO_3)_3 \bullet 6H_2O$ (98 %) $Na_2CO_3 \bullet 10H_2O$ (99 %) and dimethyl carbonate (98%) were purchased from Wako Pure Chemicals. NaOH (97 %) and *N,N*-dimethylformamide (99.5 %) were purchased from Kanto Chemicals. Glycerol (99%) was obtained from Nacalai Tesque.

Transesterification of glycerol with dimethyl carbonate:

The reaction was typically performed using 0.1 g of solid base catalyst, 2 mmol of glycerol, 10 mmol of dimethyl carbonate and 5 mL of *N,N*-dimethylformamide (DMF) as a solvent at 373 K. All experiments were carried out in a Schlenk tube attached with reflux condenser under an N_2 atmosphere. Dimethyl carbonate and DMF were distilled before use. The products were analyzed by flame ionization gas chromatography (GC-17A, Shimadzu), using a capillary column (TC-FFAP). After the reaction, 1 mmol of 1-propanol was added to the reaction solution as an internal standard. The glycerol conversion and glycerol carbonate yield were calculated as follows.

Glycerol conversion (%) = [(Initial amount of glycerol) – (amount of residual glycerol)] / (Initial amount of glycerol) × 100

Glycerol carbonate yield (%) = (amount of produced glycerol carbonate) / (initial amount of glycerol) × 100

Table S1. Transesterification of glycerol with dimethyl carbonate using hydrotalcite in polar aprotic solvents[a]

Solvent	Glycerol conversion /%	Glycerol carbonate yield /%
N,N-dimethylformamide	75	75
N,N-dimethylacetamide	56	52
Dimethyl sulfoxide	70	38
Acetonitrile	43	7

[a] Reaction conditions: glycerol (2 mmol), dimethyl carbonate (10 mmol), solvent (5 mL), hydrotalcite (Mg/Al =5, Aging time; 18 h) (0.1 g), 373 K, 1 h.

Table S2. Transesterification of glycerol with diethyl carbonate using heterogeneous and homogeneous base catalysts[a]

Catalyst	Glycerol conversion /%	Glycerol carbonate yield /%
Hydrotalcite (Mg/Al =5)	100	77
CaO	100	38
MgO	47	2
$Mg(OH)_2$	15	15
$NaHCO_3$[b]	100	69
NaOH[b]	100	54
Blank	0	0

[a] Reaction conditions: glycerol (2 mmol), diethyl carbonate (10 mmol), *N,N*-dimethylformamide (5 mL), catalyst (0.1 g), 413 K, 3 h. [b] 0.1 mmol.

For the transesterification of glycerol with dimethyl carbonate, the glycerol conversion and glycerol carbonate yield were almost the same for all samples. In contrast, there were obvious differences between glycerol conversion and glycerol carbonate yield for the reaction with diethyl carbonate operated at 413 K. This base-catalyzed transesterification involves two equilibrium steps. Climent et al. recently reported that an intermediate product, a hydroxyl alkyl carbonate was observed for transesterification of glycerol with ethylene carbonate (*J. Catal.* 2010, **269**, 140). In our experiment, an additional peak could be detected in gas chromatography analysis, which might be attributed to an intermediate product, ethyl glyceryl carbonate.

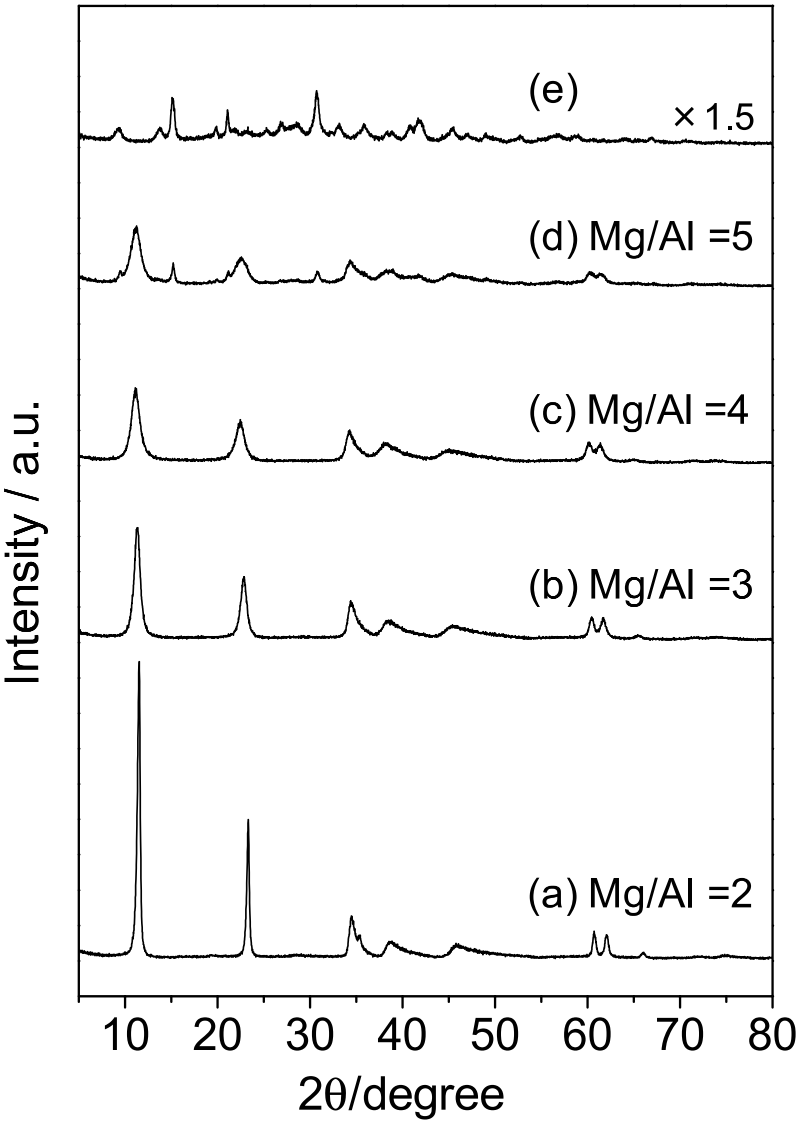

Figure S1. XRD patterns for prepared Mg-Al oxide samples with Mg/Al ratios of (a) 2, (b) 3, (c) 4 and (d) 5, and (e) hydromagnesite.