Supporting Information

Valorization of Glycerol to Glycerol Carbonate and Glycidol by Different Dialkyl Carbonates Utilizing Tricalcium Aluminate Hexahydrate as Transesterification Catalyst

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Materials

Double distilled glycerol was purchased from Molar Chemicals. Dimethyl carbonate, dipropyl carbonate and glycerol carbonate were from Sigma Aldrich with 99% purity. Diethyl carbonate and *n*-tetradecane was received from Alfa Aesar with 99% purity, dibuthyl carbonate was from TCI. Methanol was from VWR and glycidol was ordered from Acros Organics (96% purity). For the TCA synthesis, $CaCO_3$ and Al_2O_3 were Sigma Aldrich products.

Methods of structural characterization

To record powder X-ray diffractogram patterns, a Rigaku Miniflex II instrument was used, in the $\Theta = 4 – 80^{o}$ range with 2°/min scan speed using $Cu_{K\alpha}$ ($\lambda = 1.5418$ Å) radiation. The reflections were determined by the JCPDS−ICDD (Joint Committee of Powder Diffraction Standards − International Centre for Diffraction Data) database on the normalized

diffractograms. Scherrer equation was used with a shape factor of 0.9 after fitting Gaussian curves to the corresponding reflections.

Solvodynamic diameters the TCA solids were determined by dynamic light scattering measurements (Malvern NanoZS). The instrument worked with 4 mW He-Ne (λ= 633 nm) laser light source in back-scattering mode at 173°. Samples were dispersed in glycerol medium by 2 h ultrasonic irradiation, the obtained concentration was 0.5 g/dm^3.

Specific surface area were measured by a BELCAT-A catalyst analyser (Microtrac MRB) using thermal conductivity detector. Before each measurements, 100 mg of the samples were degassed at 150 °C for 3 h. Surface areas were calculated from the adsorption branches, using Brunauer-Emmett-Teller equation.

The structural attributes of the solids were defined by Fourier-transform infrared spectroscopy (JASCO FT/IR-4700 spectrophotometer equipped with ZnSe ATR accessory and DTGS detector) accumulating 128 scans with 2 cm^{-1} resolution. The spectra were analysed in the 4000 – 500 cm^{-1} wavenumber range on the normalized curves.

Thermal property of the TCA catalyst was investigated by thermogravimetric measurements applying a TA Instruments Discovery TGA device coupled with a mass spectrometer (Hiden Analytical, HPR-20 EGA). With a heating rate of 10 °C/min, the analyses were performed under permanent flow (60 mL/min) of argon containing 10% oxygen. Electron impact ionisation (70 eV energy) and Faraday cup detectors were applied to capture the ions in the (m/z) range of 1 – 300 in full scan mode. The MS transfer line (quartz inert capillary) was heated up to 200 °C and a 20 – 30 mg portion of the solids were placed in the platinum crucibles for the tests.

Morphology and elemental composition of the materials were investigated by scanning electron microscope (Hitachi S-4700) equipped with energy dispersive X-ray spectroscopy (Röntec QX2 spectrometer) at various magnifications and acceleration voltages.

Table S1. Effect of mixing rate on glycerol (Gly) conversion, glycerol carbonate (GC) and glycidol (Glycid) yields using different dialkyl carbonate solvent/reagents. Reaction conditions: 45 mg (0.12 mmol) TCA, 650 mg (7.05 mmol) glycerol and 3.5:1 DACs:glycerol molar ratio, reflux temperature, 60 min reaction time.

Stirring rate (rpm)	Dimethyl carbonate			Diethyl carbonate			Dipropyl carbonate			Dibutyl carbonate		
	Gly (%)	GC (%)	Glycid (%)	Gly (%)	GC (%)	Glycid (%)	Gly (%)	GC (%)	Glycid (%)	Gly (%)	GC (%)	Glycid (%)
1500	84.5	62.1	6.1	84.6	64.6	11.0	82.6	53.3	7.7	81.4	17.7	6.0
1000	84.0	67.1	6.5	87.4	66.8	10.5	80.8	53.1	8.2	82.2	18.5	8.2
500	85.8	59.5	6.8	83.7	61.9	8.2	78.6	54.9	8.1	77.0	17.9	5.8
250	79.4	63.7	8.0	80.1	58.3	9.6	73.4	55.7	7.0	72.8	16.1	5.3
50	74.9	59.6	7.7	76.2	58.8	8.4	69.7	52.2	6.5	71.2	14.6	7.1