Simple and efficient synthesis of cyclic carbonates using quaternized glycine as a green catalyst

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Experimental

1.1. Materials

Glycine (98.5%), 1-iodomethane (99%), and isopropanol (99.5%) were purchased from Aldrich and used without further purification. Allyl glycidyl ether (AGE) (99%) and other epoxides were also obtained from Aldrich and used as received. CO_2 of 99.999% purity was used without further purification. CH_2Cl_2 was obtained from SK Chemicals, Korea, and used as received.

1.2. Characterization

The FT-IR spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm^{-1}. The X-ray diffraction (XRD) patterns were obtained on a Philips PANalytical X'pert PRO Model power diffractometer operating at 40 kV and 30 mA using Ni-filtered Cu Kα radiation ($\lambda = 1.5404$ Å). The diffractograms were recorded in the 2θ range of 5º–50º. XPS analyses were performed using an X-ray photoelectron spectrometer (VG, ESCALAB 250) with monochromatic Al Kα radiation ($h\nu = 1486.6$ eV). Thermogravimetric analysis (TGA) was conducted using 2-4 mg of QCHT on an AutoTGA 2950 apparatus under a nitrogen flow of 100 ml/min^{-1} while heating from room temperature to 800°C at a heating rate of 10°C min^{-1}. Elemental analyses of the catalyst were carried out using a Vario EL III analyzer. For the catalyst synthesis, a multimode microwave reactor (KMIC-2KW) containing the source with a continuously adjustable power from 0 to 2 kW using a 3-stub tuner operating at a frequency of 2.450 GHz was used. The surface temperature of the reactor was measured with an IR temperature detector. The DFT calculations were performed using the gaussian 09 program at the B3LYP/6-31G (d,p) level for C, H, O, N and I.

1.3. Synthesis of cyclic carbonate from CO_2 and epoxide

For each typical batch operation, epoxide (18.6 mmol) and QGLY were placed in the reactor without solvent and then purged several times with CO_2. Next, the reactor was heated to the desired temperature, and the reaction was started by stirring the reaction mixture at 600 rpm. The cycloaddition was stopped by cooling the reaction mixture to room temperature and venting off the remaining CO_2 after the appropriate reaction time had elapsed. The product was then dissolved in dichloromethane and filtered to remove the catalyst. The product was analyzed by gas chromatography/mass spectrometry (GC-MS, Micromass, UK) analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 5.23–5.14 (2H), 5.86 (1H), 4.82–4.76 (1H), 4.49–4.45 (2H), 4.5 (2H), 4.82–4.9 (2H), and ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 154.2, 61.7, 71.8, 72, 75.1, 131.7, 115.4). The conversion of AGE and selectivity of AGC were obtained from gas chromatography data (GC; HP 6890, Agilent Technologies, Santa Clara, CA, USA).

All the reactivity test experiments were carried out twice, and if the difference of the two experimental runs exceeded 5% the third run was done before taking the average value.

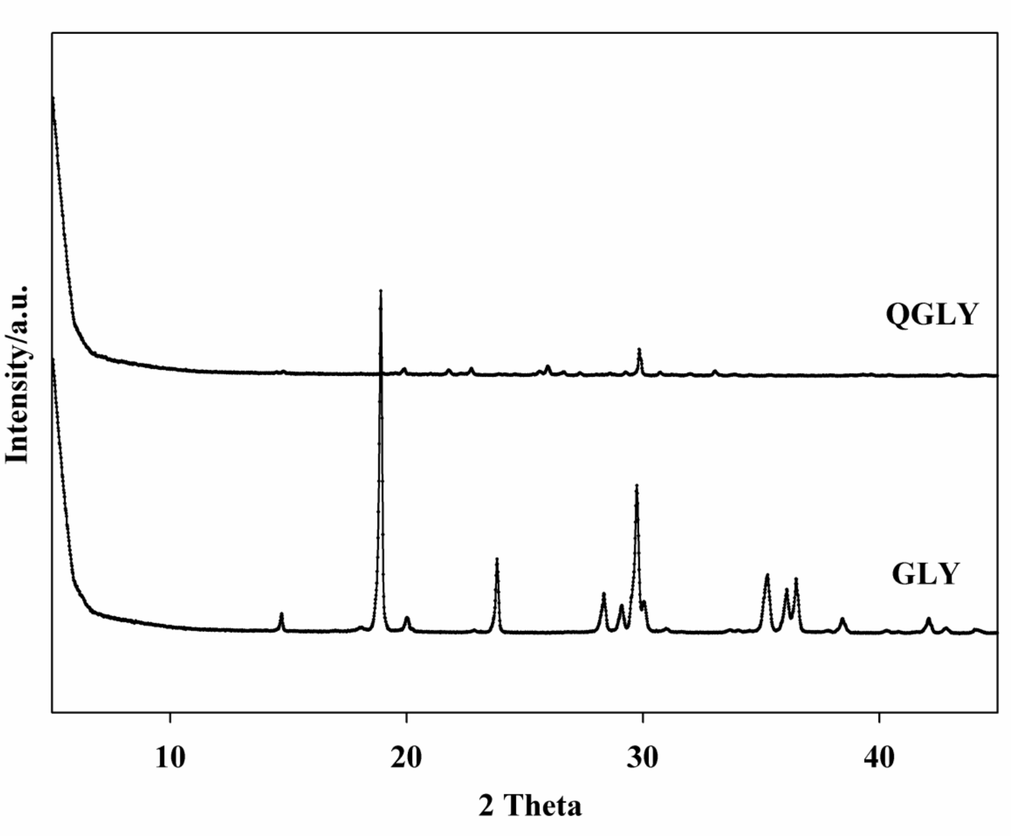


Fig. S1 XRD patterns of GLY and QGLY.

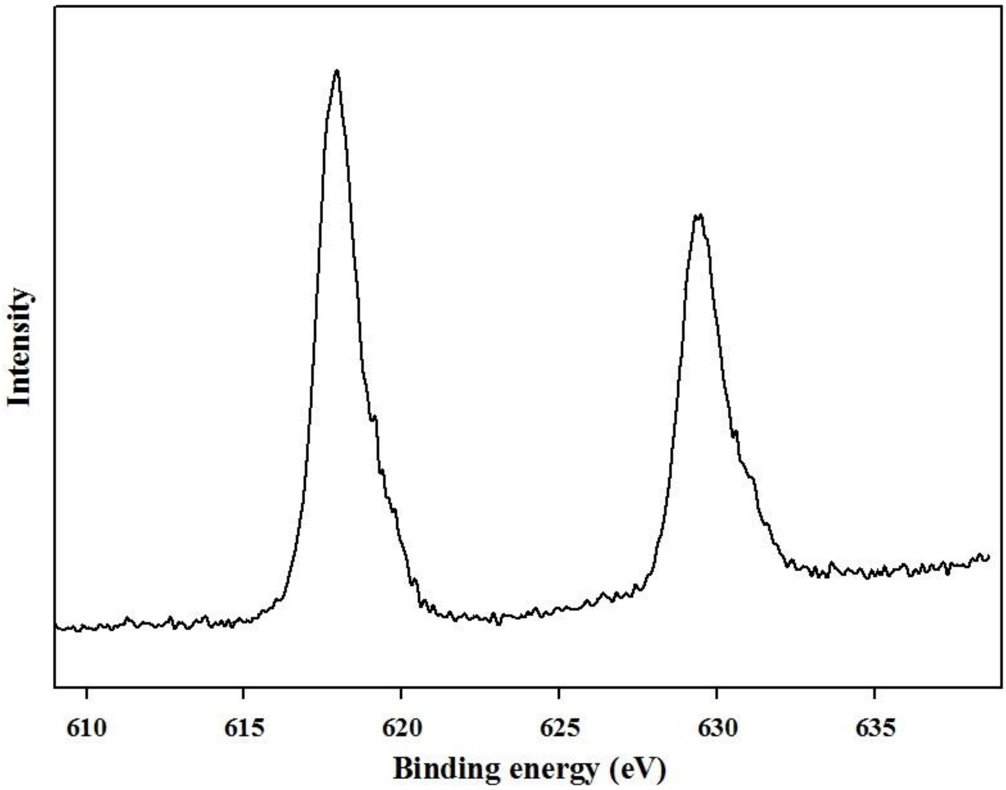
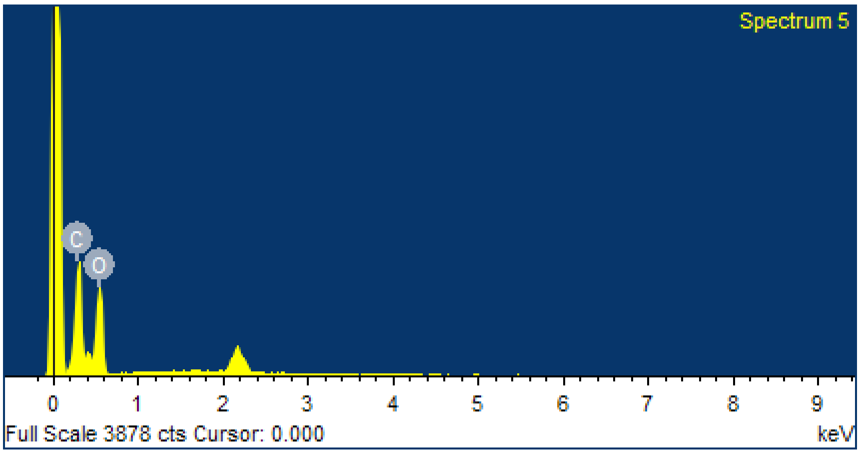


Fig. S2. XPS I 3d spectra of QGLY

GLY



QGLY

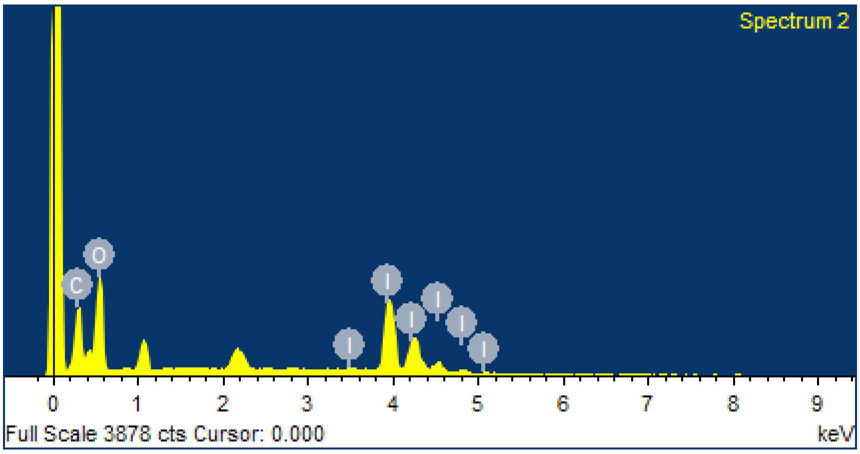


Fig. S3. EDS spectra of GLY and QGLY.

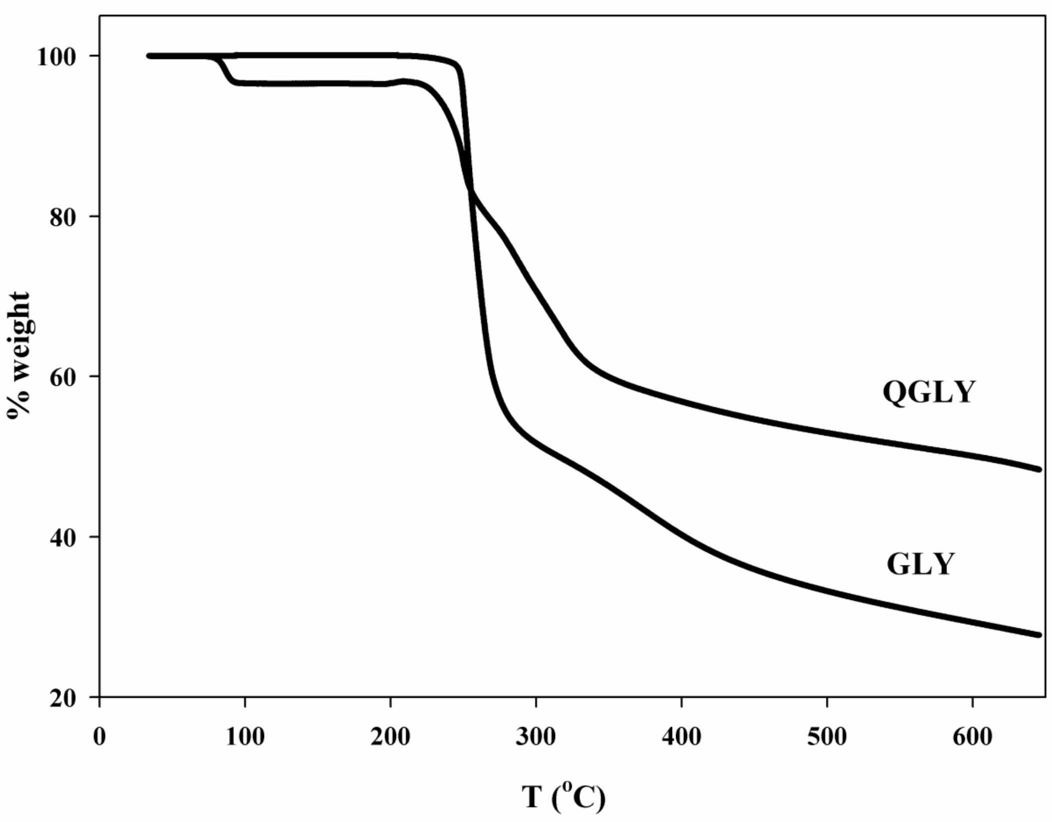


Fig. S4. TGA analysis of GLY and QGLY.

Table S1. Recycle test of QGLY.

Recycle	Conversion (%)
Fresh	94
1	94
2	93
3	84
4	75

Reaction conditions: AGE = 2.2 mL (18.6 mmol); catalyst = 0.4 mmol; time = 2 h; temp. = 120 ˚C; P_{CO2} = 1.2 MPa, selectivity = >99%.

Table S2. Elemental analysis

	C (%)	H(%)	N (%)	O (%)
GLY	31.810	6.704	17.950	42.348
QGLY	18.180	4.296	10.420	26.999