Supplementary Material (ESI) for *Energy & Environmental Science*
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An integrated approach to energy and chemicals production:

Supplementary information

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Contents

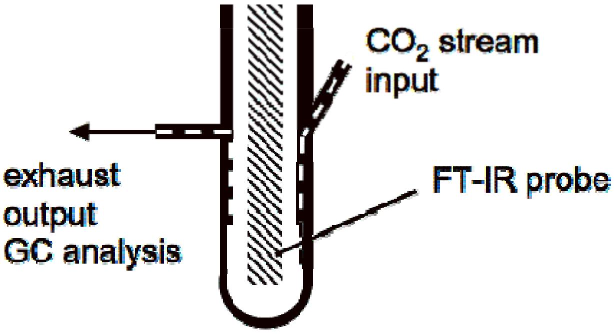
Details of chemicals and equipment

Commercially available chemicals (Alfa, Aldrich, Fluka) were used as received except that styrene oxide was freshly distilled prior to use. Glassware was dried in an oven overnight prior to use. Catalyst **1** was prepared as previously reported[S1] and it and tetrabutylammonium bromide were dried on a vacuum line at ca 50 ^{o}C for four hours prior to use. In situ IR spectra were recorded using a Varian 800 FT-IR Scimitar series spectrometer fitted with a diamond tipped ATR (3 reflections) immersion probe. Spectra were scanned between 650 and 950 cm^{-1} with 80 scans being used to obtain each time point every 5.5 minutes. Gas chromatography was performed using a Varian 3900 equipped with a thermal conductivity detector (TCD) and MolSieve 5A and HaysepQ columns with series bypass capability, helium was used as the carrier gas and analysis carried out under isothermal conditions at 90 ^{o}C. GCMS was performed on a Varian CP-800-SATURN-2200 equipped with a FactorFour (VF-5 ms) capillary column (30 m x 0.25 mm). Helium was used as the carrier gas and analysis of cyclic carbonates was carried out under the following conditions: initial temperature 60 ^{o}C, hold at initial temperature for 3 minutes, then ramp rate 15 ^{o}C min^{-1} to 270 ^{o}C; hold at final temperature for 5 minutes. EI-MS method: filament mute-delay hold for 3.50 minutes then operative in EI full scan. Data for epichlorohydrin to chloromethylethylene carbonate: T_R 5.01 min (epichlorohydrin), T_R 8.74 min (chloromethylethylene carbonate). Data for decane oxide to decane carbonate: T_R 8.99 min (decane oxide), T_R 13.38 min (decane carbonate). Data for styrene oxide to styrene carbonate: T_R 7.33 min (styrene oxide), T_R 12.09 min (styrene carbonate). Glycidol to glycerol carbonate was confirmed by ^{1}HNMR (300 MHz) due to the low volatility of glycerol carbonate.

Experimental procedure for the oxy-combustion module

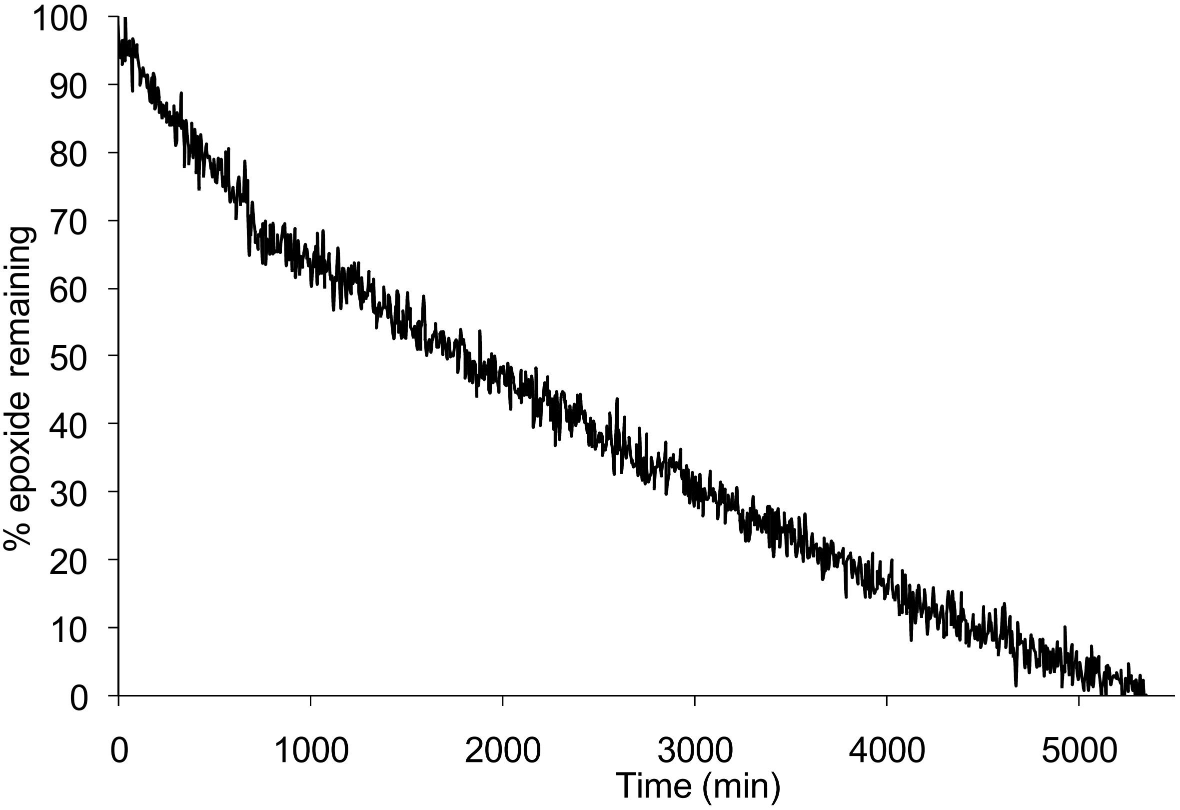
The oxy-combustion of methane (5% in helium) was carried out in a reactor module composed of four gas-tight hollow fibre $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite-type mixed ionic electronic conducting (MIEC) membranes.[S2] The membrane dimensions were; outer diameter 0.15 cm, inner diameter 0.1 cm and overall length of 20 cm. The central section within the heating zone of the furnace gave an active surface area of around 7.5 cm^{2}. The methane was flowed through the centre void (lumen) of the membranes and oxygen from the air crossed the membrane through solid-state transport to react in the lumen. Complete combustion occurred at 900 ^{o}C and provided an effluent gas composed of 5.0% CO_2 (on average) at a flow rate of 12.1-12.9 mL (STP) min^{-1}. This effluent gas was allowed to cool to room temperature and condensed water was removed. The residual gas was then passed into a reactor for cyclic carbonate synthesis (Figure 1). The reactor was placed in a thermostatically controlled bath (26 ^oC) and the contents stirred magnetically.

Length 15 cm
External diameter 3 cm
Volume 40 mL (empty)
Volume with in situ FTIR probe 15 mL

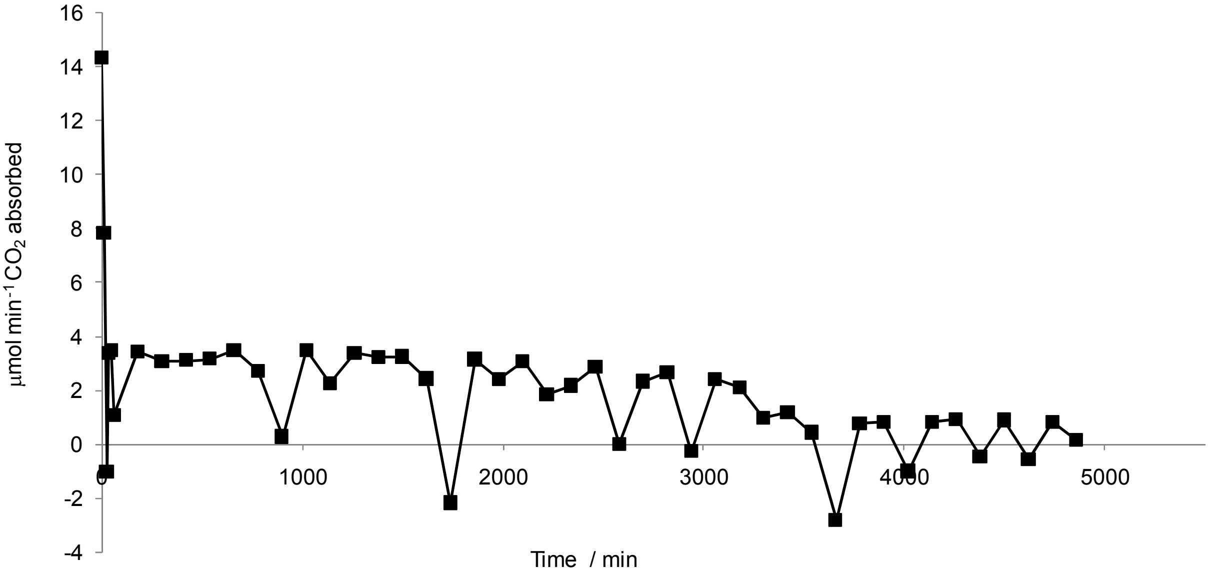


Synthesis of glycidol carbonate from glycidol

Glycidol (0.800 g, 10 mmol), catalyst **1** (0.155 g, 1.25 mol%) and TBAB (0.045 g, 1.25 mol%) were added to the reactor which was equipped with a magnetic stirrer bar and then connected to the oxy-combustion module which supplied 5.0% CO_2 (on average) at an average flow rate of 12.6 mL (STP) min^{-1}. The reactor was placed into a thermostatted bath at 26 ^oC and fitted with the *in situ* FTIR probe *via* the central B24 connector. The side taps were connected to the CO_2 stream and to the exhaust respectively. The exhaust was connected to the GC system. The reaction was monitored every 12 minutes for the first 60 minutes, then every 120 minutes by GC, and every 5.5 minutes by FTIR. Cyclic carbonate formation occurred as shown below. Cyclic carbonate synthesis was complete after between and 5300-5400 minutes, during which time approximately 9±3 mmol of CO_2 was consumed (in good agreement with the number of moles of reactant consumed).



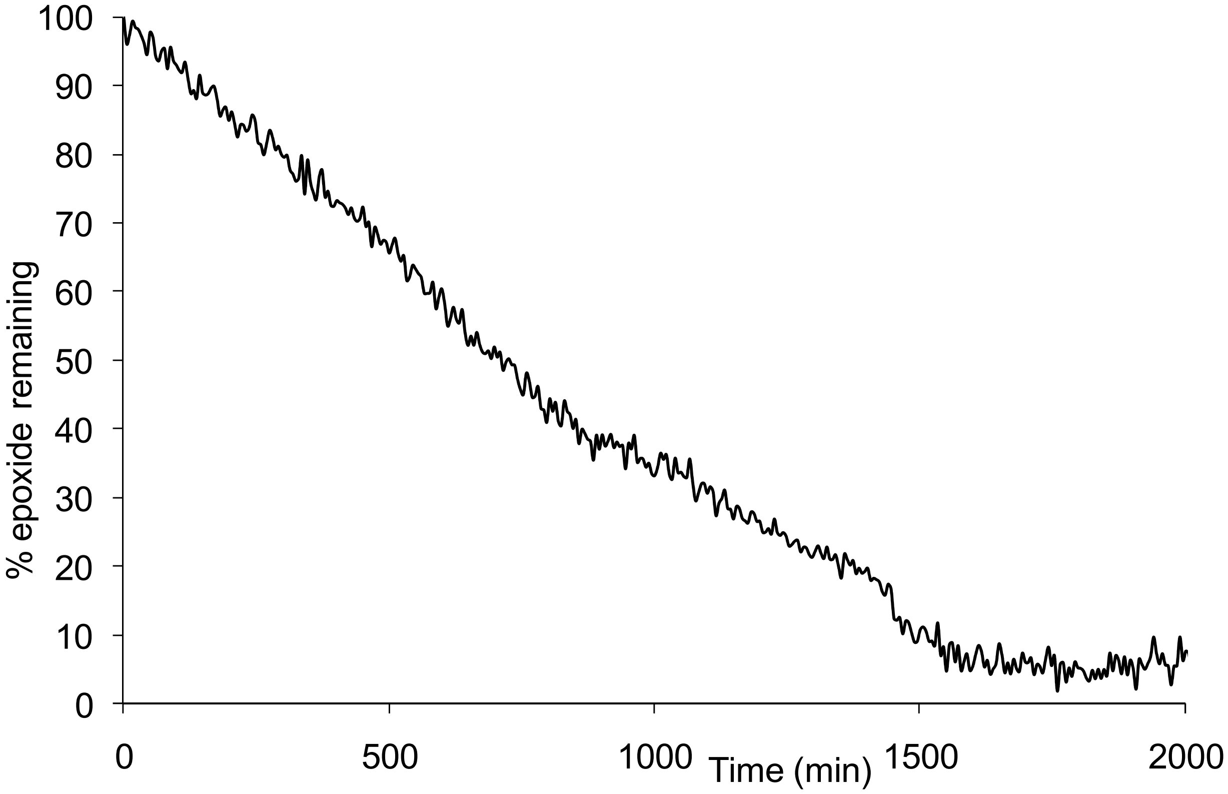
Glycidol consumption monitored by FTIR.



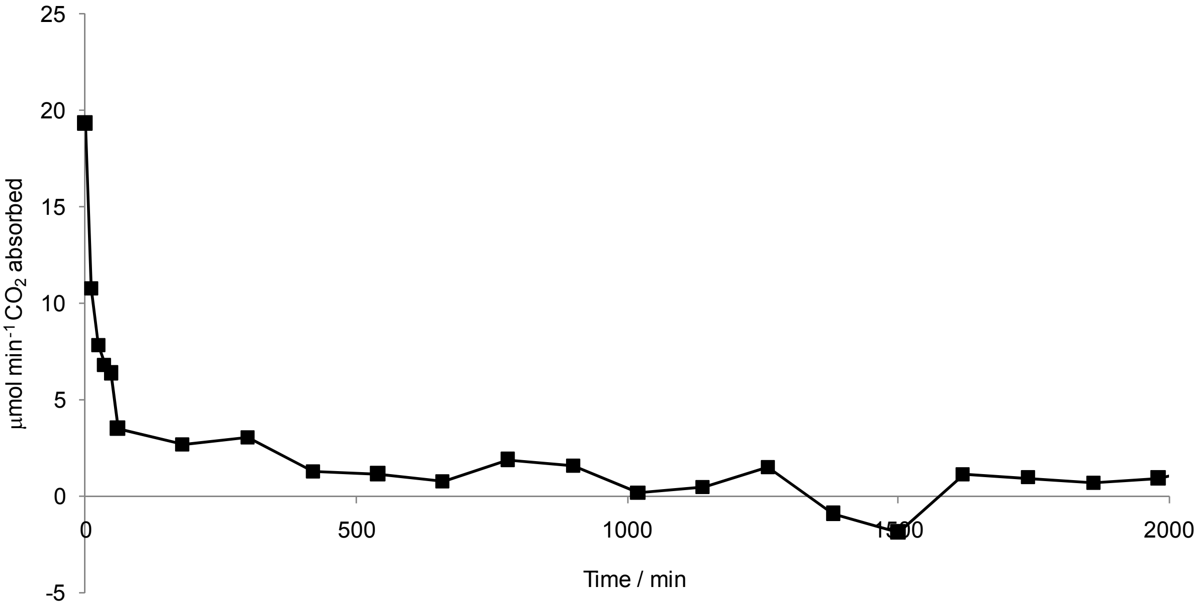
CO_2 consumption monitored by GC.

Synthesis of chloromethylethylene carbonate from epichlorohydrin

Epichorohydrin (0.805 g, 8 mmol), catalyst **1** (0.126 g, 1.25 mol%) and TBAB (0.035 g, 1.25 mol%) were added to the reactor which was equipped with a magnetic stirrer bar and then connected to the outlet of the oxy-combustion process which supplied 5.0% CO_2 (on average) at an average flow rate of 12.8 mL (STP) min^{-1}. The reactor was placed into a thermostatted bath at 26 ^{o}C and fitted with the *in situ* FTIR probe *via* the central B24 connector. The side taps were connected to the CO_2 stream and to the exhaust respectively. The exhaust was connected to the GC system. The reaction was monitored every 12 minutes for the first 60 minutes, then every 120 minutes by GC, and every 5.5 minutes by FTIR. Cyclic carbonate formation occurred as shown below. Cyclic carbonate synthesis was tending to completion after 1500-1600 minutes, during which time approximately 4±3 mmol of CO_2 were consumed (this figure is slightly lower than would be expected from the starting number of moles of epichlorohydrin but given the level of uncertainty in the intergration of the CO_2 flow with time should not be a cause for concern).



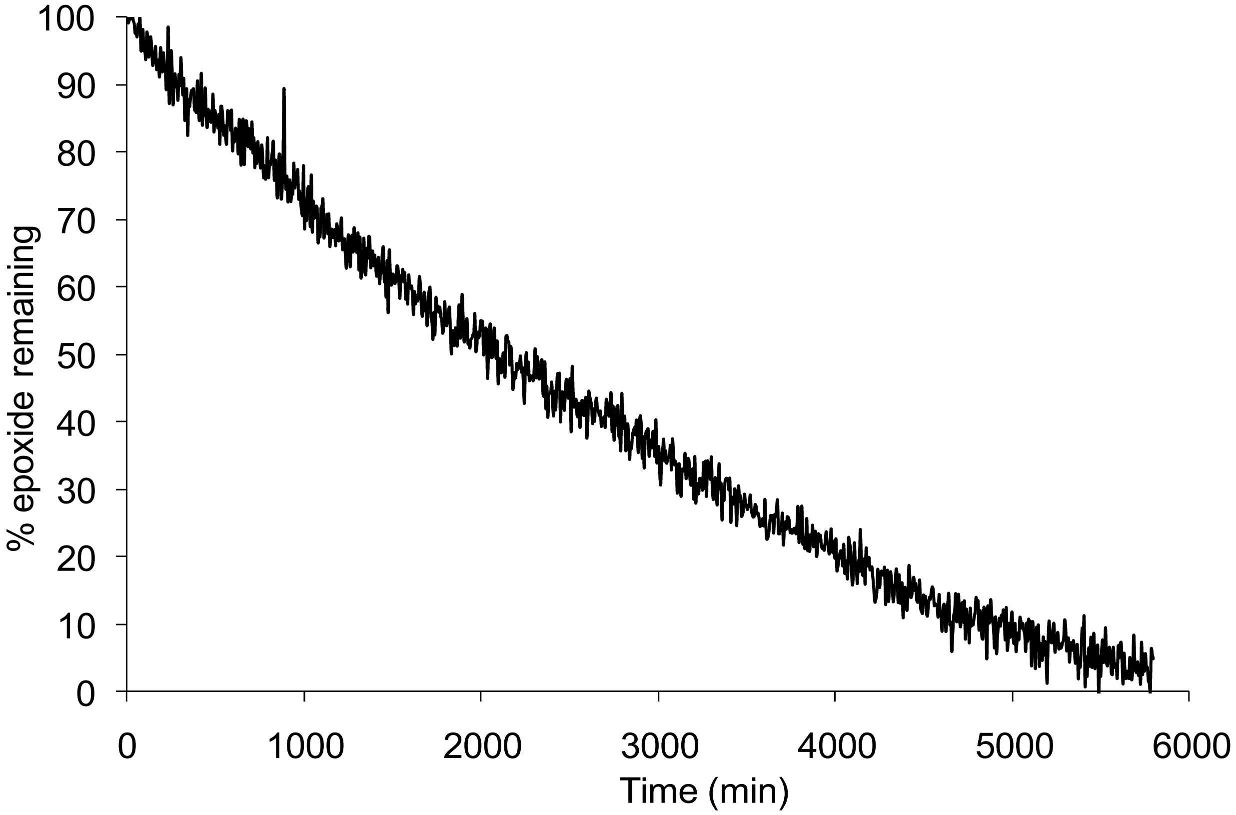
Epichlorohydrin consumption monitored by FTIR.



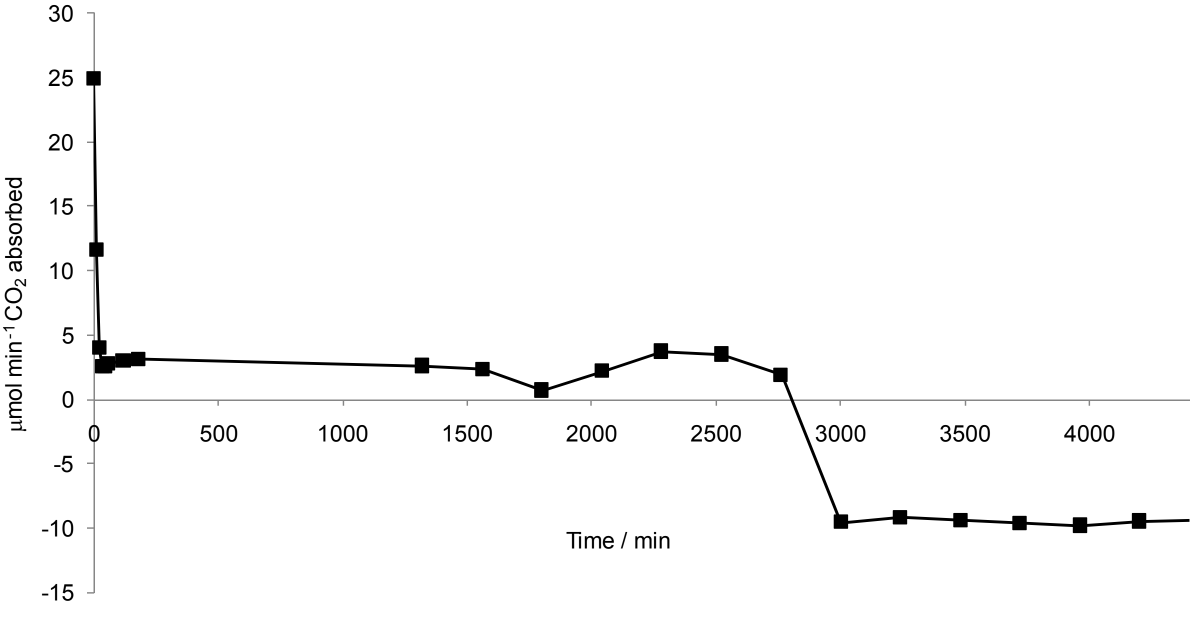
CO_2 consumption monitored by GC.

Synthesis of decane carbonate from decane oxide

Decane oxide (0.804 g, 5 mmol), catalyst **1** (0.076 g, 1.25 mol%) and TBAB (0.019 g, 1.25 mol%) were added to the reactor which was equipped with a magnetic stirrer bar and then connected to the oxy-combustion which supplied 5.0% CO_2 (on average) at an average flow rate of 12.9 mL (STP) min^{-1}. The reactor was placed into a thermostatted bath at 26 ^{o}C and fitted with the *in situ* FTIR probe *via* the central B24 connector. The side taps were connected to the CO_2 stream and to the exhaust respectively. The exhaust was connected to the GC system. The reaction was monitored every 12 minutes for the first 60 minutes, then after 120 minutes, 180 minutes and every 240 minutes from 1320 minutes to 2760 minutes by GC, and every 5.5 minutes by FTIR. Cyclic carbonate formation occurred as shown below. Cyclic carbonate synthesis was complete after 5700-5800 minutes,. During the 2760 minutes in which the reaction was monitored by GC, approximately 60% of the epoxide was converted into cyclic carbonate (i.e. 3 mmol of reactant consumed) and approximately 6±3 mmol of CO_2 consumed.



Decane oxide consumption monitored by FTIR.

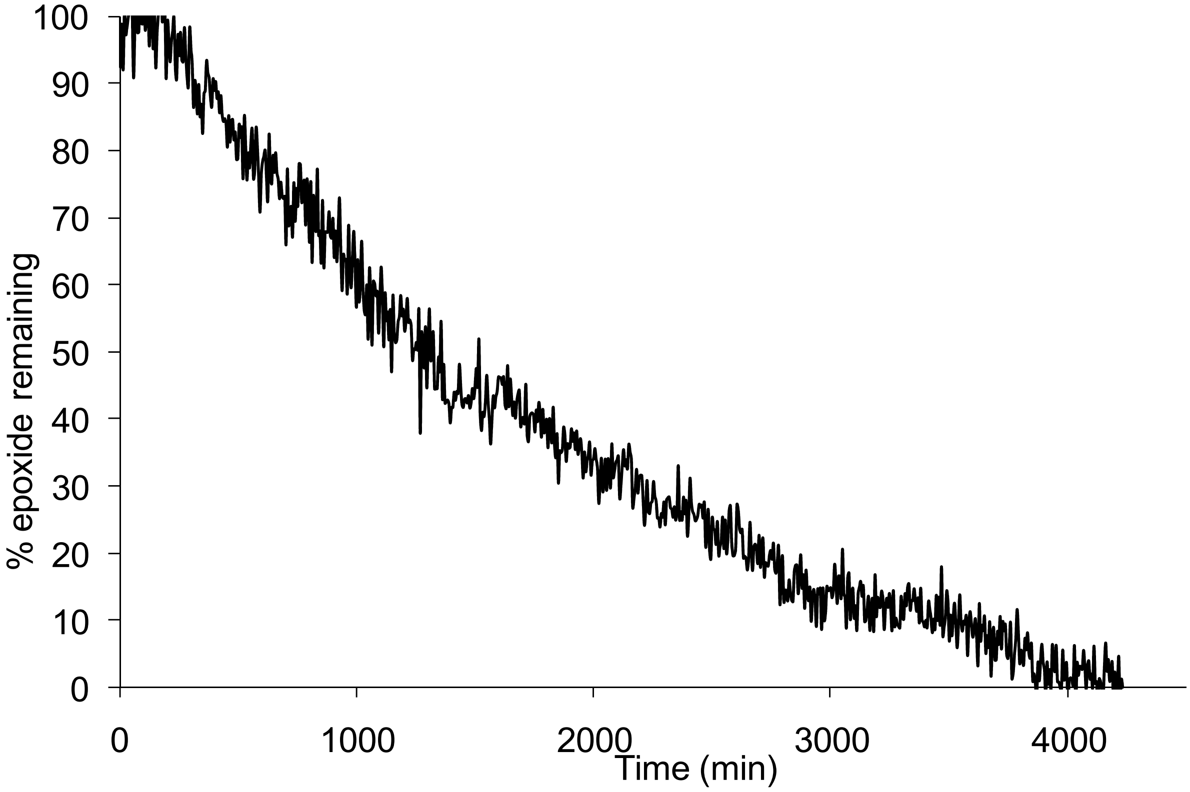


CO_2 consumption monitored by GC.

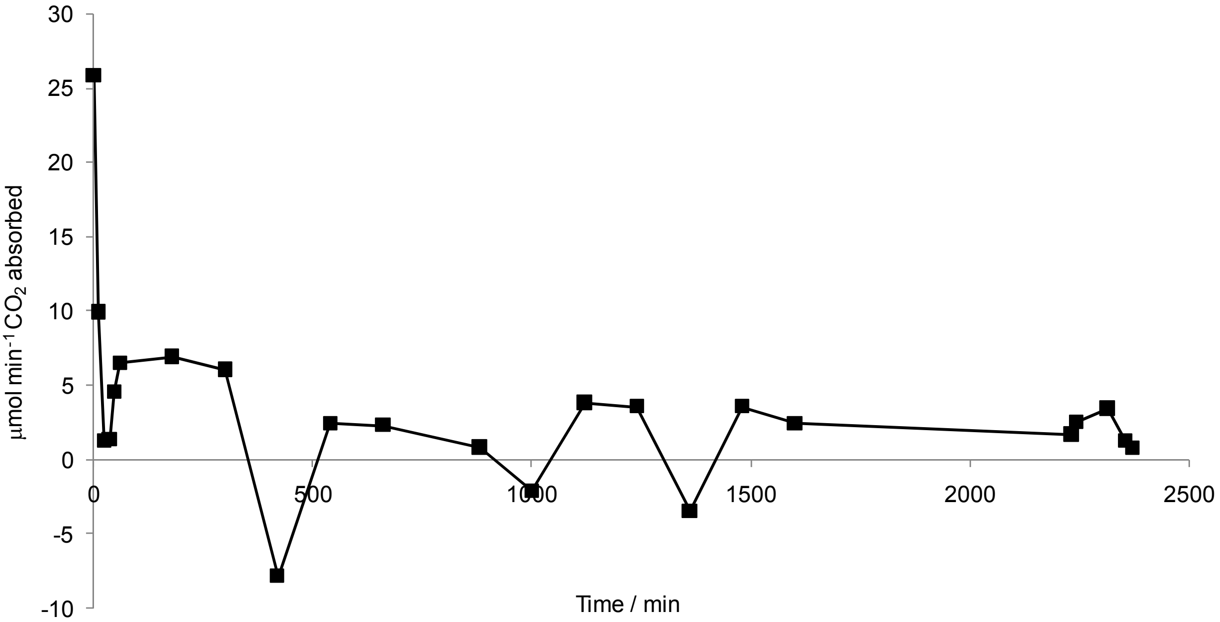
Data after 2750 minutes is not reliable owing to a leak in the system

Synthesis of styrene carbonate from styrene oxide

Styrene oxide (0.796 g, 7 mmol), catalyst **1** (0.097 g, 1.25 mol%) and TBAB (0.028 g, 1.25 mol%) were added to the reactor which was equipped with a magnetic stirrer bar and then connected to the oxy-combustion which supplied 5.0% CO_2 (on average) at an average flow rate of 12.1 mL (STP) min^{-1}. The reactor was placed into a thermostatted bath at 26 ^{o}C and fitted with the *in situ* FTIR probe *via* the central B24 connector. The side taps were connected to the CO_2 stream and to the exhaust respectively. The exhaust was connected to the GC system. The reaction was monitored every 12 minutes for the first 60 minutes, then every 120 minutes until 1620 minutes by GC, and every 5.5 minutes by FTIR. Cyclic carbonate formation occurred as shown below. Cyclic carbonate synthesis was complete after 4200-4300 minutes. During the 2369 minutes in which the reaction was monitored by GC, 75% of the epoxide (5.3 mmol) was converted into cyclic carbonate and approximately 7.5±5 mmol of CO_2 were consumed.



Styrene oxide consumption monitored by FTIR.



CO_2 consumption monitored by GC.

No data recorded after 2369 min due to instrument failure

References

S1. Meléndez, J., North, M. & Pasquale, R. Synthesis of cyclic carbonates from atmospheric pressure carbon dioxide using exceptionally active aluminium(salen) complexes as catalysts. *Eur. J. Inorg. Chem.* 3323-3326 (2007).

S2. Xiaoyao, T., Li, K., Thursfield, A. & Metcalfe, I. S. Oxyfuel combustion using a catalytic ceramic membrane reactor. *Cat. Today* **131**, 292-304 (2008).