

Supporting Information

Investigation on synthesis of dimethyl carbonate from CO₂ and ethylene oxide catalyzed by K₂CO₃ based-binary salts in the presence of H₂O

Jin-Quan Wang, Jian Sun, Chun-Yan Shi, Wei-Guo Cheng,* Xiang-Ping Zhang and

Suo-Jiang Zhang*

*State Key Laboratory of Multiphase Complex System, Institute of Process Engineering, Chinese
Academy of Sciences, P.O. Box 353, Beijing, 100190, China, Fax and Tel: (+86)-10-8262-7080,*

E-mail: sjzhang@home.ipe.ac.cn, wgcheng@home.ipe.ac.cn.

Supporting information

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1. General information

The ionic liquids were provided by Beijing zhongke anyin technology Co. Ltd. with a stated purity of >98%, and dried in vacuum for 48 h before use. The EO and organic or inorganic salts were purchased from J&KCHEMICA without further purification. GC-MS were measured on a Finnigan HP G1800 A. GC analyses were performed on a Agilent GC-6890 equipped with a capillary column (DB-624, 30 m×0.32 μm) using a flame ionization detector. NMR spectra were recorded on a Bruker 300 or Varian 400 spectrometer in CDCl₃. ¹H and ¹³C NMR chemical shifts (δ) were given in ppm relative to TMS. ¹H and ¹³C positive chemical shifts (δ) in ppm were downfield from tetramethylsilane (CDCl₃: δ_C = 77.0 ppm; residual CHCl₃ in CDCl₃: δ_H = 7.26 ppm).

The calculations were carried out by performing DFT by use of the B3PW91 functional with the 6-31++G (d, p) basis set as implemented in Gaussian 03 program package. Vibrational frequency calculations, from which the zero-point energies were derived, have been performed for each optimized structure at the same level to identify the natures of all the stationary points

2. Experiments details

2.1 Experiments details of fixation CO₂ into EC in the presence of H₂O

All CO₂ fixation reactions were conducted in a 25 mL stainlesssteel reactor equipped with a magnetic stirrer and automatic temperature control system. Typically, in the reactor, an appropriate volume of CO₂ (1.0 MPa) was added to a mixture of EO (8.8 g), H₂O (0.65), Cat1 (3.76 mmol) and Cat2 (0.9 mmol) at room temperature. The temperature was then raised to 393 K while more CO₂ was added from a reservoir tank to maintain a constant pressure (2.5 MPa). After the reaction had proceeded for 1.0 h, the reactor was cooled to 273 K in an ice water bath, and the remaining CO₂ was removed slowly. After the volatile organic products and starting materials were removed from the catalyst by distillation, the products were analyzed by GC using biphenyl as the internal standard and identified by GC-MS by comparing retention times and fragmentation

patterns with authentic samples. The product was purified by distillation or silica gel column chromatography if necessary.

2.2 Experiments details of transesterification EC with CH₃OH in the presence of EG

A mixture of EG (2 g), Cat1 (3.76 mmol), Cat2 (0.9 mmol), CH₃OH (36 g) was added to a 50 mL flask equipped with a magnetic stirrer and automatic temperature control system. The reaction was carried out for 30 min. The vessel was then cooled to room temperature. The products were analyzed by GC using biphenyl as the internal standard and identified by GC-MS by comparing retention times and fragmentation patterns with authentic samples. The product was purified by distillation or silica gel column chromatography if necessary.

2.3. Experiments details of an integrated continuous process and catalyst recycle catalyzed by KI/K₂CO₃

CO₂ fixation reactions were conducted in a 25 mL stainlesssteel reactor equipped with a magnetic stirrer and automatic temperature control system. Typically, in the reactor, an appropriate volume of CO₂ (1.0 MPa) was added to a mixture of EO (8.8 g), H₂O (0.65 g), KI (0.625 g), K₂CO₃ (0.125 g) at room temperature. The temperature was then raised to 393 K while more CO₂ was added from a reservoir tank to maintain a constant pressure (2.5 MPa). After the reaction had proceeded for 1.0 h, the reactor was cooled to 273 K in an ice water bath, and the remaining CO₂ was removed slowly. After that, 36g CH₃OH was added to mixture and transferred to a 50 mL flask equipped with a magnetic stirrer and automatic temperature control system, then reacted at 60°C for another 30min. After the vessel was then cooled to room temperature, the catalysts were distilled from the mixture and wait for another cycle.

3. Supporting NMR charts

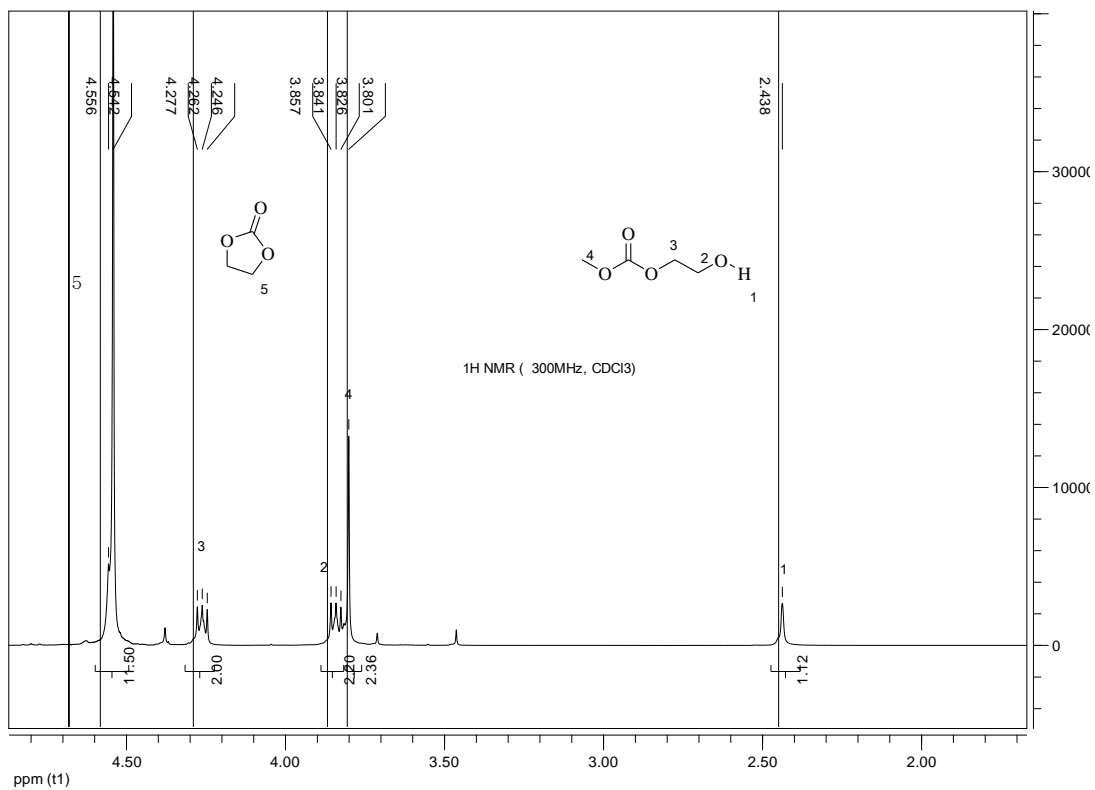


Figure S1. ¹H NMR of EC and HEMC

4.

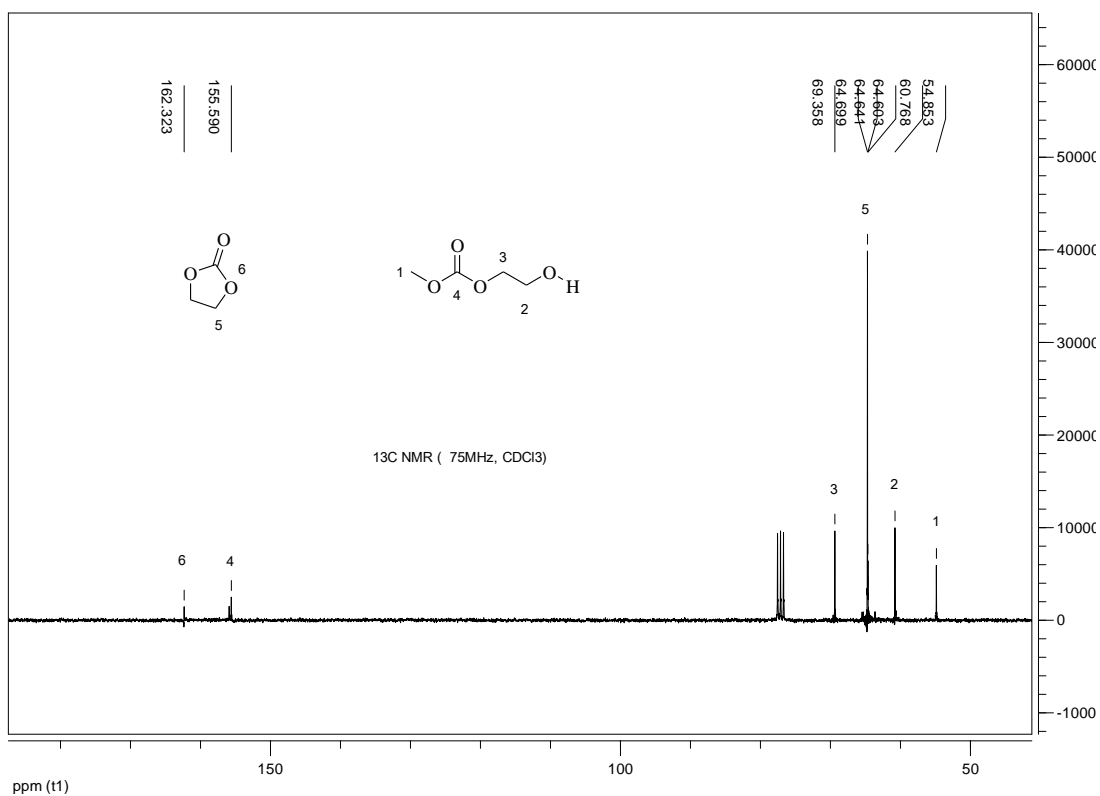


Figure S1. ¹³C NMR of EC and HEMC