Highly efficient synthesis of cyclic carbonates from CO_2 and epoxides over Cellulose/KI

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I think the revised manuscript is acceptable.

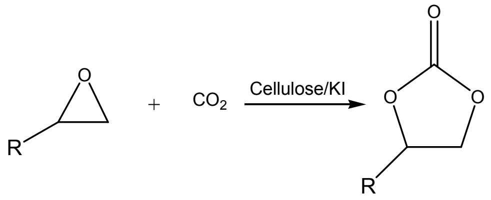
1. Experimental

CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of >99.95%. Propylene oxide, propylene carbonate, epichlorohydrin, potassium iodide, potassium bromide, potassium chloride, and all the alcohols used were analytical grade and produced by Beijing Chemical Reagents Company. Cellulose (microcrystalline) was provided by Alfa Aesar. Other epoxides were purchased from ACROS ORGANICS. All chemicals were used without further purification.

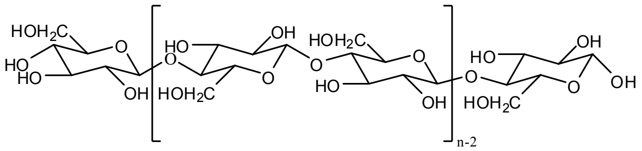
To prepare the cellulose/KI catalyst, a desired amount of cellulose was dispersed in an aqueous solution of KI. The solution was stirred for about 1 h at 303 K. Then the water was evaporated under reduced pressure, and dried under vacuum at 333 K for 24 h.

All the cycloaddition reactions were conducted in a stainless steel reactor of 22 mL equipped with a magnetic stirrer, which was similar to that used previously.[1] We describe the procedures for the cycloaddition of PO because the procedures for other reactions were similar. In the experiment, desired amount of catalyst and PO was added into the reactor. The reactor was sealed and put into a constant-temperature air bath of desired temperature. CO_2 was then charged into the reactor until desired pressure was reached, and the stirrer was started. After a certain time, the reactor was placed into ice water and CO_2 was released slowly passing through a cold trap containing ethanol to absorb the trace amount of reactant and product entrained by CO_2. After depressurization, ethanol in the cold trap and internal standard n-butanol were added into the reactor. The reaction mixture was analyzed by GC (Agilent 6820) equipped with a flame-ionized detector and a capillary column (PEG-20M, 30 m). To study the reusability of the catalyst, the catalyst was washed using ethyl ether to remove the product and n-butanol, and then dried under vacuum for 12 h at 333 K before reuse. The products of the other cycloaddition reactions were analyzed at room temperature on a Bruker 400 MHz ^1H NMR spectrometer using $CDCl_3$ as the solvent.

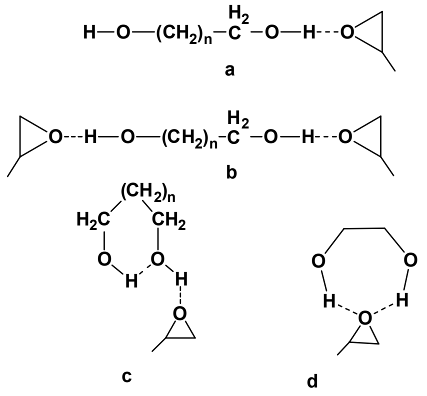
2. Results and discussions



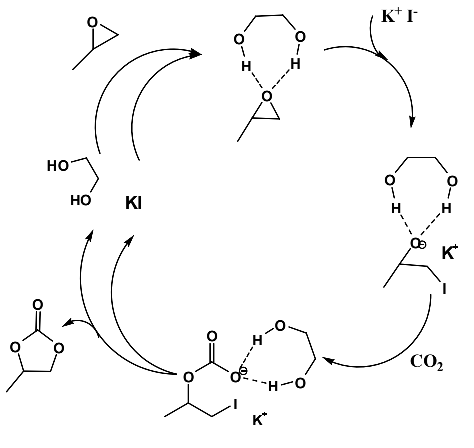
Scheme S1. Cycloaddition reaction of CO_2 and epoxides



Scheme S2. The molecular structure of cellulose



Scheme S3. The possible ways of hydrogen bonding between the diols with PO ($n \geq 1$)



Scheme S4. Proposed mechanism of the cycloaddition reaction in the presence of vicinal diols.

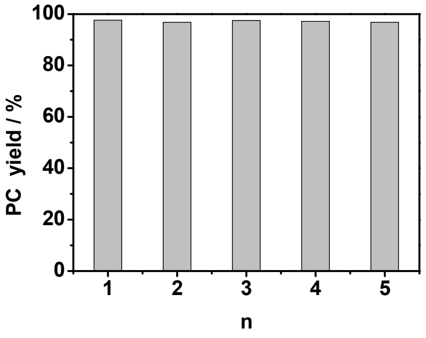
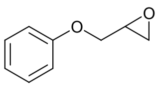
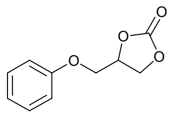
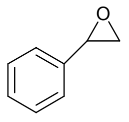
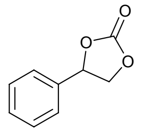
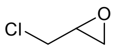
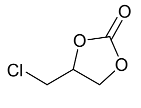


Figure S1. Reuse of the catalyst. Reaction conditions: temperature 383 K, pressure 2 MPa, reaction time 1.5 h, PO 20 mmol, 0.2 g cellulose/KI catalyst with 66 wt% cellulose

Table S1 Synthesis of various carbonates from CO_2 and epoxides catalyzed by cellulose/KI [a]

Entry	Epoxides	Products	Reaction time (h)	Yield (%)
1	 1b	 2b	4.5	99
2	 1c	 2c	9	98
3	 1d	 2d	10.5	92

[a] Reaction conditions: 20 mmol epoxide, CO_2 pressure 2 MPa, reaction temperature 383 K, 0.2 g cellulose/KI catalyst with 66 wt% cellulose.

^{1}H NMR spectra of glycol and 1,2-propanediol with and without PO The signal of the H atom in hydroxyl group shifts to the downfield in ^{1}H NMR spectra after hydrogen bonding.[2] The hydrogen bonding of PO with glycol and 1,2-propanediol was studied using ^{1}H NMR technique. The spectra of glycol and 1,2-propanediol with and without PO are given in Figures S2 and S3, respectively. Obviously, the diols can form hydrogen bonds with PO. For 1,2-propanediol, after adding PO, the signal of H atom in the OH shifts to the downfield and split into 2.65 ppm and 2.56 ppm because the chemical environments of the two H atoms are different.

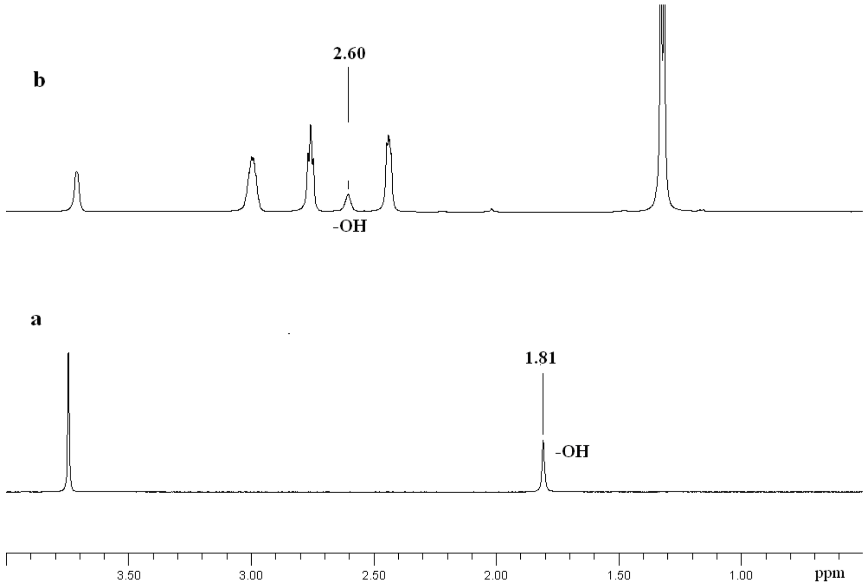


Figure S2. The ^{1}H NMR of glycol with and without PO;

a) glycol 2 μL, $DCCl_3$ 0.5 mL;

b) glycol 2 μL, PO 20 μL, $DCCl_3$ 0.5 mL.

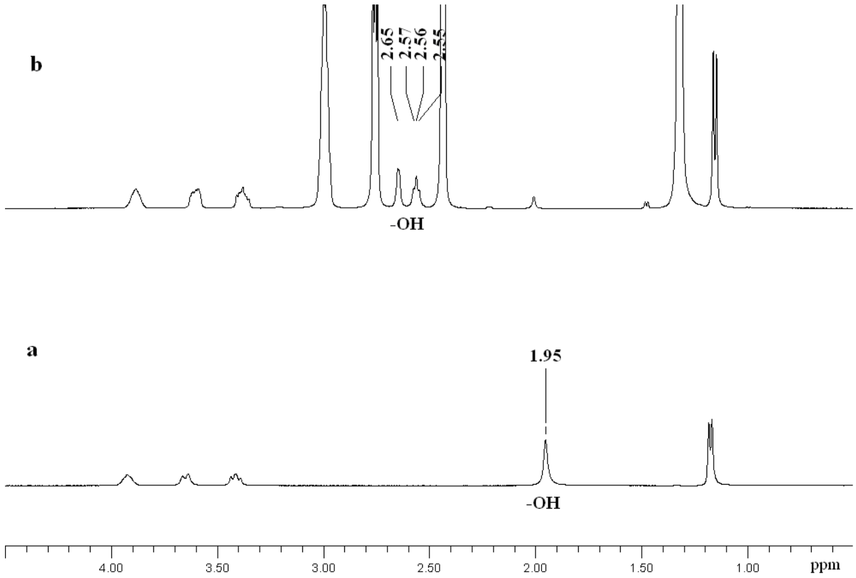


Figure S3. The ^{1}H NMR of 1,2-propanediol with and without PO;

a) 1,2-propanediol 2 μL, $DCCl_3$ 0.5 mL;

b) 1,2-propanediol 2 μL, PO 20 μL, $DCCl_3$ 0.5 mL.

References

1 H. Z. Liu, T. Jiang, B. X. Han, S. G. Liang and Y. X. Zhou, *Scinece* 2009, **326**, 1250-1252.

2 J. S. Lomas, C. Cordier, *J. Phys. Org. Chem.,* 2009, **22**, 289-297.