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Journal Name

ARTICLE TYPE

C$_{60}$ fullerenol as an active and stable catalyst for synthesis of cyclic carbonates from CO$_2$ and epoxides

Yong-Bin Sun, Chang-Yan Cao*, Shu-Liang Yang, Pei-Pei Huang, Chun-Ru Wang and Wei-Guo Song*

C$_{60}$ fullerenol was found to be a highly active, selective and stable catalyst for cycloaddition between CO$_2$ and epoxides to produce various cyclic carbonates with excellent yields (89−99 %). A solid/liquid interfacial hydrogen-bond assisted
10 **mechanism was proposed to account for its high efficiency.**

Carbon dioxide (CO$_2$) is a nontoxic, nonflammable, and naturally abundant C1 feedstock for several organic reactions.[1-5] The development of viable method to activate and use CO$_2$ to prepare useful chemicals and materials has received much attention in
15 decades.[6] One of the most successful examples is the synthesis of cyclic carbonates from CO$_2$ and epoxides (Scheme 1).[7] The cyclic carbonates are very useful as polar aprotic solvents, synthetic epoxides and raw materials for engineering plastics.[8] They are also key precursor to produce dimethyl carbonate, which is
20 important electrolyte in lithium ion batteries.[9] So far, various homogeneous and heterogeneous catalysts have been developed for the coupling reaction between CO$_2$ and epoxides to produce cyclic carbonates. These catalysts include quaternary ammonium and phosphoniumsalts,[10, 11] ionic liquids,[12] alkali metal salts,[13]
25 salen complexes,[14, 15] N-heterocyclic carbenes,[16] and heterogeneous nanomaterials including MgO,[9] Mg-Al metal oxides,[17] Fe(OH)$_3$,[18] and so on. However, unsatisfactory activities, low stabilities of catalysts are still two major hurdles needed to be overcome. Thus highly effective and stable catalysts are desirable
30 and we found one such catalyst in C$_{60}$ fullerenol.
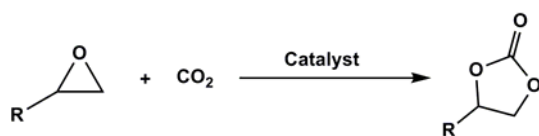
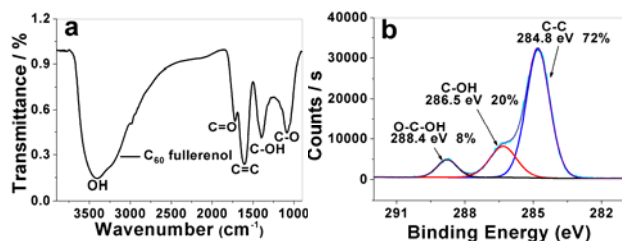**Scheme 1** Cycloaddition reaction of CO$_2$ and epoxides to produce cyclic carbonates.

As a model reaction, the cycloaddition reaction between
35 propylene oxide and CO$_2$ has been intensively studied. In a mechanistic study, Sakakura et al. reported that the catalytic activity of phosphonium salts could be enormously enhanced by synergistically promotions of the weakly acidic surface silanol groups.[19] Zhang et al. reported that hydroxyl group together with
40 traditional ionic liquid catalysts could efficiently catalyze this reaction without Lewis acid.[20] Han et al. reported that the compounds with the hydroxyl group could act as co-catalysts to accelerate the reaction, and the catalyst efficiency was higher

after the intramolecular hydrogen bond was formed.[21] In our
45 previous study, flowerlike Fe$_3$O$_4$/amorphous Fe(OH)$_3$ core/shell nanocomposites with abundant surface hydroxyl groups also showed impressive activity and stability for this reaction.[18] These studies suggest that hydrogen-bonding between catalyst and epoxide could be a key factor in inducing the cycloaddition
50 reaction between epoxide and CO$_2$.

C$_{60}$ fullerenol, as a polyhydroxylated fullerene derivative, has up to forty hydroxyl groups per one fullerene molecule, and it has attracted much attention in biochemistry, medicinal and catalytic applications.[22, 23] For example, Song et al. reported that C$_{60}$
55 fullerenol was an outstanding catalyst for Henry reaction, Aldol reaction, Michael addition reaction and Friedel-Crafts reaction, showing desirable features of both homogeneous catalysis and heterogeneous catalysis.[24] With above studies, we envisioned that C$_{60}$ fullerenol may be a good catalyst for the cycloaddition
60 reaction between epoxide and CO$_2$.

Herein, we report that C$_{60}$ fullerenol was indeed a highly active, selective and stable catalyst for cycloaddition CO$_2$ with various epoxides to produce cyclic carbonates. A solid/liquid interfacial hydrogen-bond assisted mechanism was proposed to clarify its
65 high efficiency.

C$_{60}$ fullerenol was prepared from pristine C$_{60}$ by oxidation with ozone and hydroxylation with hydrogen peroxide according to the literatures with minor modifications[25] (detail synthesis procedure was shown in ESI†). FTIR spectrum of as-prepared C$_{60}$ fullerenol
70 is shown in Fig. 1a. A broad band at around 3400 cm^{-1}, which can be assigned to hydroxyl groups (-OH) appeared on IR spectrum. Other three bands at 1080 cm^{-1}, 1370 cm^{-1}, and 1620 cm^{-1} can be assigned to ν_{C-O}, δs_{C-O-H}, and $\nu_{C=C}$ absorptions, respectively. These four broad bands are similar to most reported C$_{60}$ fullerenol,
75 indicating that synthesis of C$_{60}$ fullerenol was successfully.[26] XPS results further confirmed that C$_{60}$ fullerenol had abundant hydroxyl groups. As shown in Fig. 1b, C 1s spectrum of C$_{60}$ fullerenol can be divided into three peaks. The peak with a binding energy at 284.8 eV (72 %), 286.5 eV (20 %) and 288.4
80 eV (8 %) could be assigned to nonoxygenated carbon (C-C), monoxygenated carbon (C-OH), and hemiketal carbon (O-C-OH),[27] respectively. Based on the XPS and elemental analysis data (Table S1), the average molecular formula of C$_{60}$ fullerenol in this study was determined to be C$_{60}$(OH)$_{17}$O$_5$•28H$_2$O.

Fig. 1 (a) FTIR spectrum of C_{60} fullerenol, (b) XPS spectra of the C1s of C_{60} fullerenol and the fitted peaks.

The catalytic activity of C_{60} fullerenol was first tested for cycloaddition reaction of CO_2 and propylene oxide (PO) with KI as co-catalyst. The propylene carbonate (PC) yield was 3.2 % when using KI only, and the PC yield was 0.3 % when using C_{60} fullerenol only. However, when C_{60} fullerenol and KI were added together, the PC yield reached 95 % within 2 h, as shown in Fig. 2a. These results indicate the excellent synergetic effect of C_{60} fullerenol and KI for catalyzing the reaction.
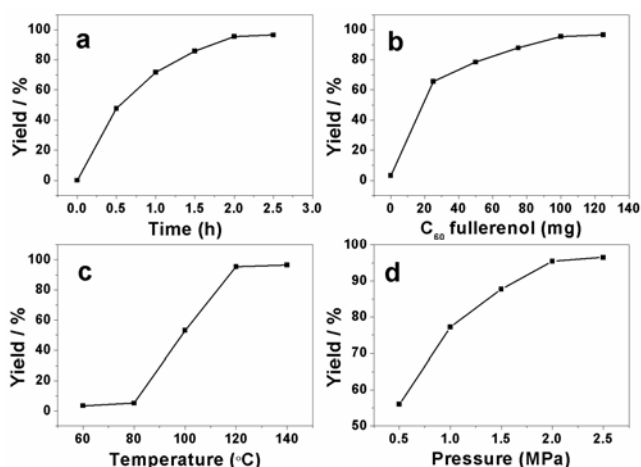

Fig. 2 The effect of the reaction conditions on the yield of PC (100 mmol PO, 1 mmol KI); (a) the effect of reaction time on the yield of PC, reaction conditions: CO_2 pressure 2 MPa, C_{60} fullerenol 100 mg, temperature 120 ºC; (b) the effect of C_{60} fullerenol amount on the yield of PC, reaction conditions: CO_2 pressure 2 MPa, time 2 h, temperature 120 ºC; (c) the effect of reaction temperature on the yield of PC, reaction conditions: CO_2 pressure 2 MPa, C_{60} fullerenol 100 mg, time 2 h; (d) the effect of reaction pressure on the yield of PC, reaction conditions: time 2 h, C_{60} fullerenol 100 mg, temperature 120 ºC.

The reaction parameters were optimized regarding the amount of catalyst, reaction temperature and pressure, etc. Under otherwise identical reaction conditions, the PC yield increased with increasing amount of C_{60} fullerenol, as shown in Fig. 2b.[28] Therefore, all of the results discussed below were obtained using 100 mg C_{60} fullerenol. The yield of PC on temperature is shown in Fig. 2c. The higher reaction temperature increases the reactivity of the epoxide, but the solubility of the CO_2 gas in the reaction system decreases with increasing temperature.[29] Fig. 2d shows the effect of CO_2 pressure on the yield of PC at 120 ºC. When the CO_2 pressure increased from 0.5 MPa to 2.0 MPa, the PC yield increased from 56% to 95%. A higher CO_2 pressure can effectively increase the solubility of CO_2 in the reaction system, thus result in an acceleration of the cyclic carbonate formation.[30] These results indicate that the catalytic system is very efficient for this reaction.

C_{60} fullerenol catalyst is a heterogeneous catalyst in this cycloaddition reaction. With its abundant hydroxyl groups, C_{60} fullerenol can be dispersed well in reaction system. The separation of the catalyst from the reaction mixture is quite easy via centrifugation. The stability of the catalyst was examined. As shown in Fig. 3, no obvious decrease of the PC yield was observed after ten cycles, indicating that the catalyst was very stable. FTIR spectrum of C_{60} fullerenol after being reused for ten times was nearly the same as the fresh one (Fig. S2, ESI†). Such stability was impressive, as coke species are prone to be formed under high temperature and pressure used in this study. TEM images showed that only small size change of C_{60} fullerenol after being reused (Fig. S3, ESI).

The stability of the C_{60} fullerenol catalyst was likely due to the C_{60} cage that itself was very stable. We envisioned that the C_{60} fullerenol molecules were bound together through hydrogen bonds between hydroxyl groups so that they behaved like solid heterogeneous catalyst. However, such hydrogen bonds were weak and reversible, so that the C_{60} fullerenol molecules may also behave like homogeneous catalyst in certain ways, including less coking formation and less deactivation.
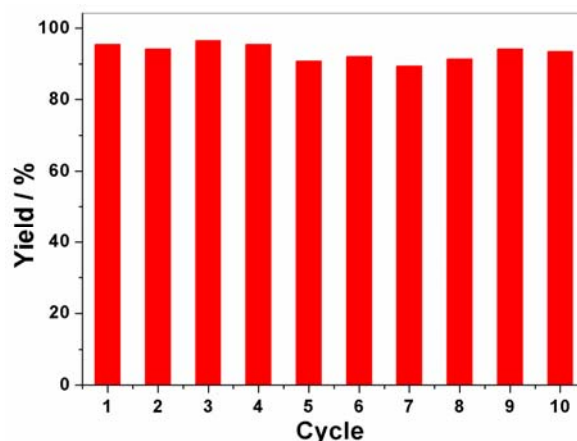
Fig. 3 Recycling results of the fresh C_{60} fullerenol and fullerenol after 10 times reused.

The cycloaddition of CO_2 with other epoxides with C_{60} fullerenol as catalyst was also studied at 120 ºC and 2.0 MPa (Table 1). The data showed that C_{60} fullerenol was effective for a variety of terminal epoxides, producing the corresponding cyclic carbonates with high yields of 89~99 %. The cyclohexane oxide exhibited lower activity (entry 7), probably due to the high steric hindrance of the cyclohexane ring.[31]

Zhang et al. proposed that hydroxyl groups in the catalyst had synergetic effect with the halide anion for the cycloaddition reaction between epoxide and CO_2.[28] Song et al. reported that nanostructured materials rich in hydroxyl groups provide Lewis-acid sites through surface hydroxyl groups while KI provide nucleophilic groups.[18] In this study, C_{60} fullerenol provide Lewis acid site to active the oxygen atom in the epoxide ring through its hydroxyl groups, and KI as the nucleophilic group to activate the carbon atom in the epoxide ring.

On the basis of these results, we propose a solid/liquid interfacial hydrogen-bond assisted mechanism for the cycloaddition reaction between epoxide and CO_2 with C_{60} fullerenol as catalyst. As shown in Fig. 4, the hydroxyl group on

the surface of C_{60} fullerenol acts as a weak acid, activating the epoxide through a hydrogen bond, and I$^-$ anion made a nucleophilic attack on the less sterically hindered carbon on epoxide, resulting in ring-opening. Then the interaction occurred
[5] between the oxygen anion of the ring-opening epoxide and CO_2, forming an alkylcarbonate anion, which transformed into a cyclic carbonate by the intramolecular substitution of I$^-$ in the next step.

Table 1 Carbonate synthesis catalyzed by C_{60} fullerenol in the presence of KI.[a]

Entry	Epoxide	Product	Time (h)	Yield (%)	TON	TOF (h^{-1})
1			8	99	1576	197
2			15	97	1545	103
3			22	90	1433	65
4			6	98	1561	260
5			7	91	1449	207
6			5	99	1576	315
7			24	89	1417	59

[10]

[a]Reaction conditions: epoxide (100 mmol), C_{60} fullerenol 100 mg, KI 1 mmol, CO_2 2 MPa, 120 °C.
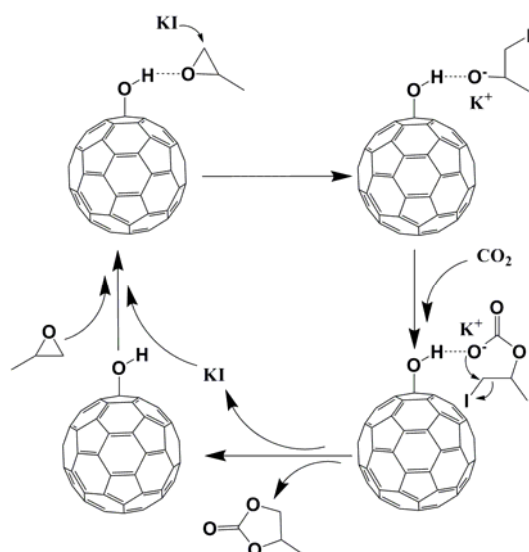
Fig. 4 Mechanism of the hydrogen-bond assisted cycloaddition of CO_2
[15] and epoxide at the solid/liquid interface, catalyzed by KI and fullerenol.

In summary, we demonstrated that C_{60} fullerenol was an excellent catalyst for the synthesis of propylene carbonate from propylene oxide and CO_2. Hydrogen-bonding at the solid/liquid interface was crucial for high activity of catalysts rich in surface
[20] hydroxyl groups. C_{60} fullerenol could be reused for ten times without loss of activity, and was applicable to a variety of terminal epoxides.

Notes and references

CAS Key Laboratory of Molecular Nanostructures and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Tel&Fax: 86 10-62557908
[30] *E-mail: cycao@iccas.ac.cn, wsong@iccas.ac.cn*

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