

**Electronic Supplementary Information**

**Fabrication of solid strong bases with a molecular-level dispersion  
of lithium sites and high basic catalytic activity**

Lin-Bing Sun,\* Jie Shen, Feng Lu, Xiao-Dan Liu, Li Zhu and Xiao-Qin Liu

*State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and  
Chemical Engineering, Nanjing Tech University, Nanjing 210009, China*

\*Corresponding author. E-mail: lbsun@njtech.edu.cn.

## Experimental Section

### Materials.

The grafting of lithium *tert*-butoxide [LiO<sup>t</sup>Bu]<sub>4</sub> (LTB) onto CD was conducted as follows. Dry CD (0.3g) was suspended in benzene (60 mL) under an Ar atmosphere, followed by addition of the molecular precursor LTB. The white suspension was stirred at 25 °C for 1 h. The solid was recovered by filtration and washing with benzene for three times, so that a clear filtrate was obtained. The yielded white powder was dried in vacuum at 25 °C for 0.5 h, 50 °C for 0.5 h, and 60 °C for 2.5 h. The resultant materials were denoted as Li-CD-1, Li-CD-2, and Li-CD-3, corresponding to a lithium content of 0.8, 1.8, and 2.5 mmol g<sup>-1</sup>, respectively.

As a comparison, the sample (Li/Al<sub>2</sub>O<sub>3</sub>) with the same lithium content as Li-CD-3 was prepared by the conventional method. LiNO<sub>3</sub> (0.1 g) was dissolved in water (10 mL) followed by addition of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.2 g). After stirring at the room temperature for 24 h, water was evaporated from the mixture. The obtained solid was dried in an oven at 100 °C and the intermediate LiNO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> was formed. The intermediate was calcined under an Ar flow at 600 °C for 2 h. After that the sample Li/Al<sub>2</sub>O<sub>3</sub> was formed. In a similar process, Li/SiO<sub>2</sub> was prepared by impregnating LiNO<sub>3</sub> into SiO<sub>2</sub> and calcination at 600 °C.

### Characterization.

X-ray diffraction (XRD) patterns of samples were recorded using a Bruker D8 Advance diffractometer with Cu K $\alpha$  at 40 kV and 40 mA. Fourier transform infrared (IR) spectra of the samples diluted with KBr were performed on a Nicolet Nexus 470 spectrometer. <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AV600 spectrometer at room temperature.

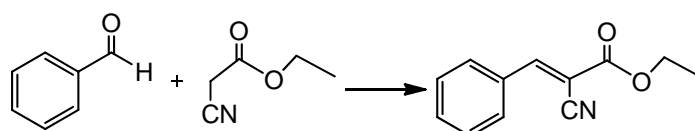
The content of Li was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 2000DV, PerkinElmer). To measure the amount of basic sites, 50 mg of the sample was added into 10 mL of aqueous HCl (0.05 M). The sample suspension was shaken for 24 h and the slurry was separated by a centrifuge. The remained acid in liquid phase was titrated with standard base (0.01 M aqueous NaOH) and phenolphthalein was

employed as an indicator. The amount of HCl consumed was used to calculate the amount of basic sites. Thermogravimetric (TG) analysis was performed on a thermobalance (STA-499C, NETZSCH). About 10 mg of sample was heated from the room temperature to 700 °C in a flow of air.

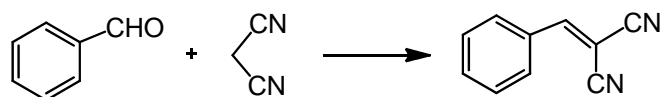
### Catalytic test.

Diethyl carbonate (DEC) was synthesized from the transesterification of ethylene carbonate and ethanol. In a typical process, ethanol (0.5 mol), ethylene carbonate (0.1 mol), and catalyst (0.5 wt% of ethanol) were added to a three-necked glass flask with a water-cooled condenser. The reaction was conducted at 80 °C with stirring for a given period of time. After the reaction was completed, the reaction mixtures were recovered from the flask and subjected to centrifuging. The obtained upper liquid was then analyzed by a Varian 3800 gas chromatography equipped with a flame ionization detector.

Catalytic activity was assessed through the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate (Scheme 1) or malononitrile (Scheme 2). In a typical experiment, benzaldehyde (8 mmol), ethyl cyanoacetate (8 mmol) and ethanol (solvent, 5 mL) were added to a 25 mL round-bottomed flask reactor equipped with a condenser under nitrogen atmosphere. After the heating temperature was adjusted to 70 °C, the solid catalyst (0.1 g) was added into the reactor, and then the reaction slurry was stirred for 2.5 h under reflux. After reaction, n-dodecane (0.85 g) was added into the above system as the internal standard to calculate the reaction conversion. Then the reaction mixture was centrifuged to remove the solid catalyst, and the liquid phase was analyzed by a gas chromatography equipped with a flame ionization detector.

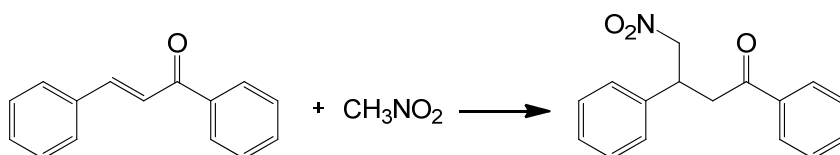


**Scheme S1** Knoevenagel reaction of benzaldehyde with ethyl cyanoacetate.



**Scheme S2** Knoevenagel condensation of benzaldehyde with malononitrile.

Catalytic activity was also assessed through the Michael addition reaction (Scheme S3). A mixture of 1,3-diphenyl-2-propenone (2 mmol), nitromethane (2 mmol) and catalyst (0.1 g) in methanol (10 mL) was heated at 60°C under reflux for 6 h. After cooling to room temperature, the solvent was removed in vacuo, and the oily residue obtained was partitioned between ethyl acetate (20 mL) and H<sub>2</sub>O (20 mL). The organic layer was separated, dried over sodium sulfate, and evaporated under reduced pressure. The crude product was subjected to chromatography on silica gel eluted with petroleum ether/ether. The final product used for the calculation of yield was examined by NMR.



**Scheme S3** Michael addition of chalcone with nitromethane.

Table S1. Knoevenagel condensation of benzaldehyde (**A**) with malononitrile (**B**)

Catalyst	Reaction conditions	Yield (%)	Reference
N-MCM-48 <sup>a</sup>	10 mmol <b>A</b> , 8 mmol <b>B</b> , 50 mg catalyst, 60 °C, 3 h	78	1
TBD/MCM-41 <sup>b</sup>	1 mmol <b>A</b> , 1 mmol <b>B</b> , 5 mg catalyst, 70 °C, 2 h	95	2
CsX	Certain amount of <b>A</b> and <b>B</b> , 5 wt% catalyst, 60 °C, 1 h	91	3
MgO	10 mmol <b>A</b> , 8 mmol <b>B</b> , 50 mg catalyst, 60 °C, 3 h	72	1
MgO-MCM-41 <sup>c</sup>	40 mmol <b>A</b> , 40 mmol <b>B</b> , 150 mg catalyst, 80 °C, 4 h	93	4
MgO-MCM-41-N <sup>d</sup>	40 mmol <b>A</b> , 40 mmol <b>B</b> , 150 mg catalyst, 80 °C, 4 h	99	4
mp-PBI <sup>e</sup>	1 mmol <b>A</b> , 1 mmol <b>B</b> , 50 mg catalyst, 100 °C, 6 h	100	5
Li-CD-3	8 mmol <b>A</b> , 8 mmol <b>B</b> , 100 mg catalyst, 70 °C, 2.5 h	100	This work

<sup>a</sup> N-incorporated mesoporous silica MCM-48; <sup>b</sup> 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) immobilized on mesoporous silica MCMC-41; <sup>c</sup> MgO loaded mesoporous silica MCM-41; <sup>d</sup> N-incorporated MgO-MCM-41; <sup>e</sup> Mesoporous poly(benzimidazole).

Table S2. Knoevenagel condensation of benzaldehyde (**A**) with ethyl cyanoacetate (**C**)

Catalyst	Reaction conditions	Yield (%)	Reference
TBD/MCM-41 <sup>a</sup>	1 mmol <b>A</b> , 1 mmol <b>C</b> , 5 mg catalyst, 70 °C, 2 h	54	2
NH <sub>2</sub> -MCM <sup>b</sup>	20 mmol <b>A</b> , 20 mmol <b>C</b> , 250 mg catalyst, 82 °C, 36 h	94	6
MCM41OH <sup>c</sup>	10 mmol <b>A</b> , 8 mmol <b>C</b> , 80 mg catalyst, 60 °C, 2 h	77	7
CsX	Certain amount of <b>A</b> and <b>C</b> , 5 wt% catalyst, 60 °C, 1 h	7	3
MgO	Certain amount of <b>A</b> and <b>C</b> , 5 wt% catalyst, 60 °C, 1 h	80	3
Hydrotalcite	10 mmol <b>A</b> , 10 mmol <b>C</b> , 110 mg catalyst, 60 °C, 4 h	94	8
Li-CD-3	8 mmol <b>A</b> , 8 mmol <b>C</b> , 100 mg catalyst, 70 °C, 2.5 h	97	This work

<sup>a</sup> 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) immobilized on MCMC-41; <sup>b</sup> Aminopropyl-functionalized MCMs; <sup>c</sup> Tetraalkylammonium hydroxide anchored on MCM-41.

Table S3. Michael addition of chalcone (**D**) with nitromethane (**E**)

Catalyst	Reaction conditions	Yield (%)	Reference
NP <sup>a</sup>	1 mmol <b>D</b> , 1 mmol <b>E</b> , 0.1 g catalyst, 65 °C, 6 h	25	9
KF/NP <sup>a</sup>	1 mmol <b>D</b> , 1 mmol <b>E</b> , 0.1 g catalyst, 65 °C, 6h	60	9
KF/CP <sup>b</sup>	1 mmol <b>D</b> , 1 mmol <b>E</b> , 30 mg catalyst, 45 °C, 5 h	70	10
MgAlO- <sup>t</sup> Bu <sup>c</sup>	2 mmol <b>D</b> , 2 mmol <b>E</b> , 0.1 g catalyst, RT, 0.16 h	93	11
Ba(OH) <sub>2</sub>	2 mmol <b>D</b> , 2 mmol <b>E</b> , 0.1 g catalyst, RT, 20 h	95	11
KF/Al <sub>2</sub> O <sub>3</sub>	5 mmol <b>D</b> , 5 mmol <b>E</b> , 4 g catalyst, 25 °C, 2 h	96	12
Li-CD-3	2 mmol <b>D</b> , 2 mmol <b>E</b> , 0.1 g catalyst, 60 °C, 6 h	88	This work

<sup>a</sup> Natural phosphate; <sup>b</sup> Clinoptilolite; <sup>c</sup> *tert*-Butoxide anion incorporated into the interlayer of hydrotalcite.

## References

- 1 Y. Xia and R. Mokaya, *Angew. Chem. Int. Ed.*, 2003, **42**, 2639.
- 2 Y. V. S. Rao, D. E. De Vos and P. A. Jacobs, *Angew. Chem. Int. Ed.*, 1997, **36**, 2661.
- 3 M. J. Climent, A. Corma, S. Iborra and A. Velty, *J. Mol. Catal. A: Chem.*, 2002, **182–183**, 327.
- 4 T. Wang, G. Wu, N. Guan and L. Li, *Microporous Mesoporous Mater.*, 2012, **148**, 184.
- 5 P. Makowski, J. Weber, A. Thomas and F. Goettmann, *Catal. Commun.*, 2008, **10**, 243.
- 6 D. J. Macquarrie and D. B. Jackson, *Chem. Commun.*, 1997, 1781.
- 7 I. Rodriguez, S. Iborra, F. Rey and A. Corma, *Appl. Catal., A*, 2000, **194–195**, 241.
- 8 M. J. Climent, A. Corma, S. Iborra, K. Epping and A. Velty, *J. Catal.*, 2004, **225**, 316.
- 9 M. Zahouily, B. Bahlaouan, M. Aadil, A. Rayadh and S. Sebti, *Org. Process. Res. Develop.*, 2004, **8**, 275.
- 10 H. Keipour, M. A. Khalilzadeh, A. Hosseini, A. Pilevar and D. Zareyee, *Chin. Chem. Lett.*, 2012, **23**, 537.
- 11 B. M. Choudary, M. L. Kantam, B. Kavita, C. V. Reddy and F. Figueras, *Tetrahedron*, 2000, **56**, 9357.
- 12 D. E. Bergbreiter and J. J. Lalonde, *J. Org. Chem.*, 1987, **52**, 1601.

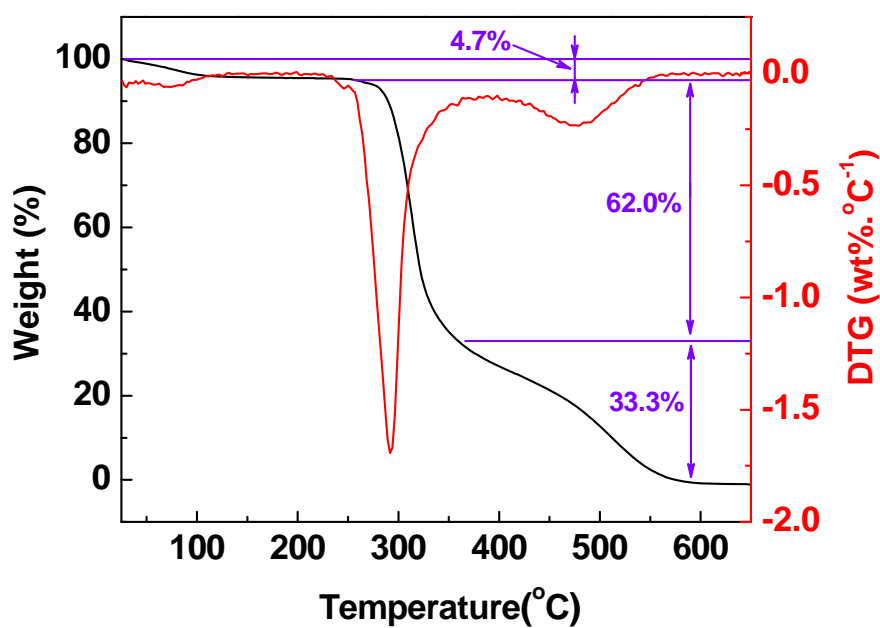


Figure S1. TG and DTG curves of the pristine CD.

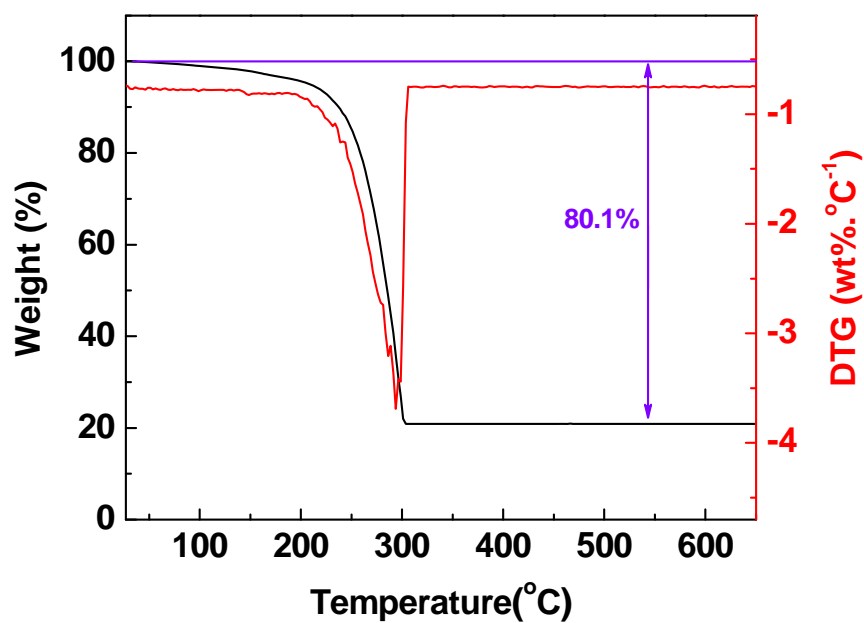
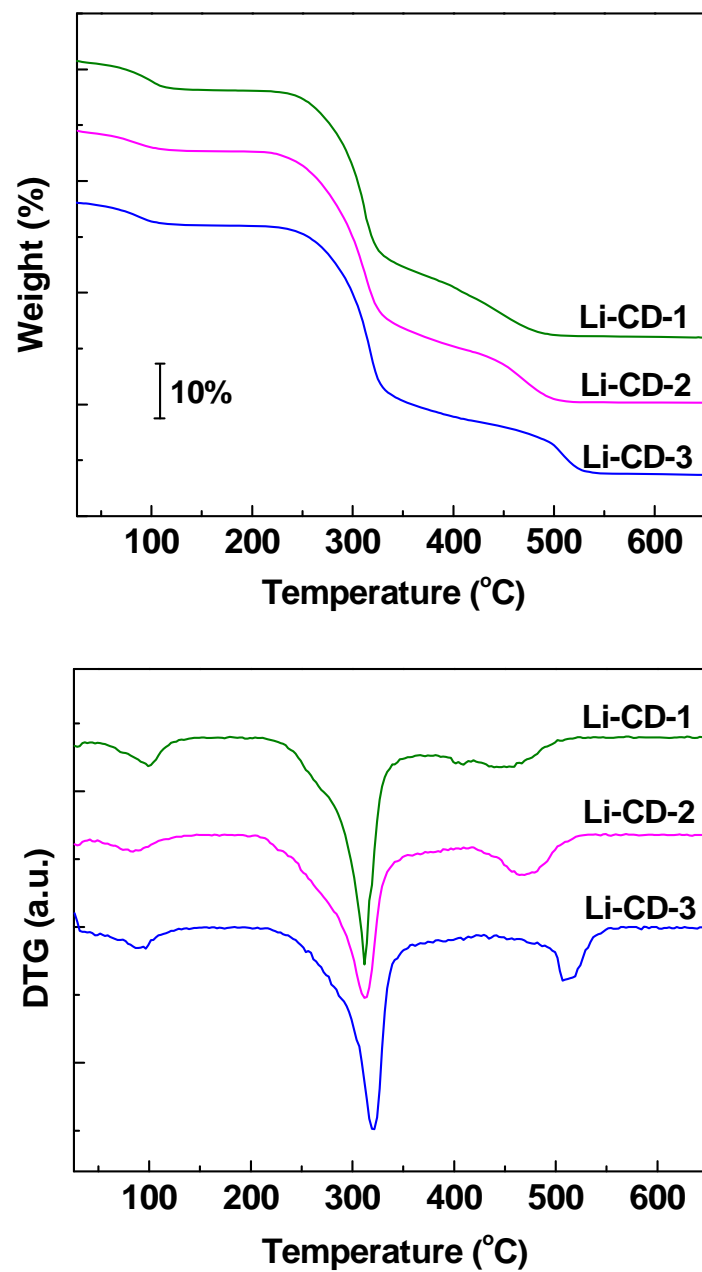
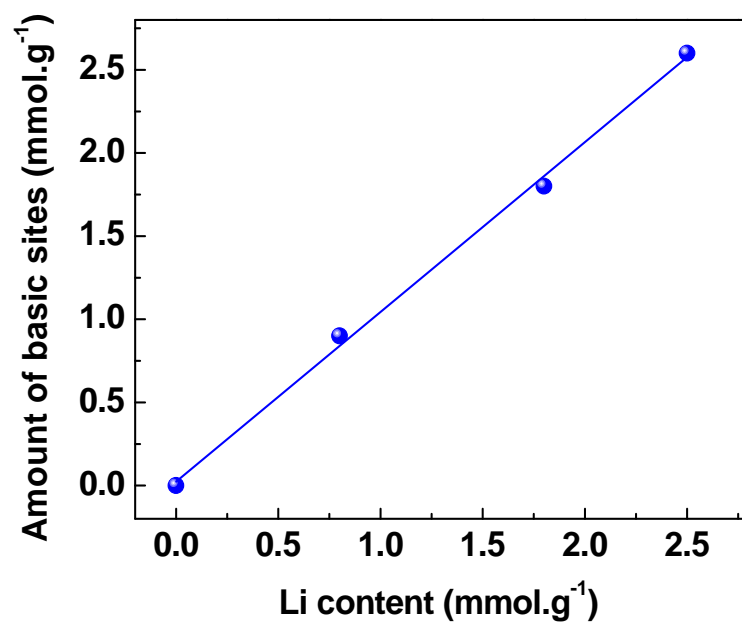


Figure S2. TG and DTG curves of the precursor LTB.



**Figure S3.** TG and DTG curves of Li-CD-1, Li-CD-2 and Li-CD-3 samples. Curves are plotted offset for clarity.





**Figure S4.** Amount of basic sites as a function of lithium content of different samples.