

## Supporting Information

### **Isolated Lithium Sites Supported on Mesoporous Silica: A Novel Solid Strong Base with High Catalytic Activity**

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## Experimental Section.

### Materials Preparation.

Mesoporous silica SBA-15 was synthesized as follows. The triblock copolymer P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , 3g) was dissolved in water (22.5 g) and 2 M HCl aqueous solution (90 g) with stirring at 40 °C. Then tetraethylorthosilicate (TEOS, 6.38 g) was added to the homogeneous solution and stirred at 40 °C for 24 h. The resulting mixture was transferred to a Teflon-lined autoclave and kept at 140 °C for 24 h. The obtained solid product was filtered, washed, and air-dried at room temperature followed by calcination at 550 °C in an air flow for 5 h.

The grafting of lithium *tert*-butoxide  $[\text{LiO}^t\text{Bu}]_4$  (LTB) onto the silanol groups in SBA-15 was conducted as follows. Dry SBA-15 (0.2 g) was suspended in benzene (20 mL) under an Ar atmosphere, followed by addition of the molecular precursor LTB (0.3, 0.6, 1.0, 1.3, and 1.6 mmol). 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 and colorless 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 LiS-*x*, where *x* ranges from 1 to 5, corresponding to the samples derived from 0.3-1.6 mmol of LTB as described above. Elemental analysis shows that lithium contents in the final samples increase gradually from LiS-1 to LiS-4, while keep constant with further increase of lithium precursor dosage (Table S1). That means, lithium has been successfully introduced into SBA-15, and the maximum loading is about  $6.5 \text{ mmol}\cdot\text{g}^{-1}$  for the host used in the present study.

As a comparison, a sample ( $\text{Li}_2\text{O}/\text{SBA-15}$ ) with the same composition as LiS-4 was prepared by the conventional method.  $\text{LiNO}_3$  (0.1 g) was dissolved in water (10 mL) followed by addition of SBA-15 (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  $\text{LiNO}_3/\text{SBA-15}$  was formed. The intermediate was calcined under an air flow at 600 °C for 2 h. After that the sample  $\text{Li}_2\text{O}/\text{SBA-15}$  was formed.

## Characterization.

X-ray diffraction (XRD) patterns of the materials were recorded using a Bruker D8 Advance diffractometer with monochromatic Cu  $K_{\alpha}$  radiation in the  $2\theta$  range from  $0.7^{\circ}$  to  $5^{\circ}$  and  $5^{\circ}$  to  $70^{\circ}$  at 40 kV and 40 mA. Transmission electron microscopy (TEM) was performed on a JEM-2010 UHR electron microscope operated at 200 kV.  $N_2$  adsorption-desorption experiments were carried out using an ASAP 2020 system at  $-196^{\circ}\text{C}$ . The sample was treated at  $60^{\circ}\text{C}$  for 12 h prior to measurement. The Brunauer-Emmet-Teller (BET) surface area was estimated using the adsorption branches in the relative pressure range from 0.04 to 0.20. The total pore volume was calculated using the amount adsorbed at a relative pressure of about 0.99. The pore size distribution was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method.

Fourier transform infrared (IR) measurements were carried out on a Nicolet Nexus 470 spectrometer with a spectra resolution of  $2\text{ cm}^{-1}$  using transparent KBr pellets. Thermogravimetry (TG) analysis was conducted on a thermobalance (STA-499C, NETZSCH). About 10 mg of sample was heated from the room temperature to  $900^{\circ}\text{C}$  in a flow of air or nitrogen ( $25\text{ mL}\cdot\text{min}^{-1}$ ). The content of Li was measured by 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.

## Catalytic Test.

Dimethyl carbonate (DMC) was synthesized from the transesterification reaction, in which ethylene carbonate and methanol were used as starting materials. In a typical process, methanol (0.5 mol), ethylene carbonate (0.1 mol), and a catalyst (0.5 wt% of methanol) were added to a three-necked glass flask. The reaction was conducted at  $65^{\circ}\text{C}$  with stirring for 0.5-4 h. After the

reaction was finished, the reaction mixture was recovered from the flask and subjected to centrifuging. The obtained upper liquid was then analyzed by use of a Varian 3800 gas chromatography equipped with a flame ionization detector.

**Table S1. Lithium Content, Textural Parameters, and Basic Properties Different Samples <sup>a</sup>**

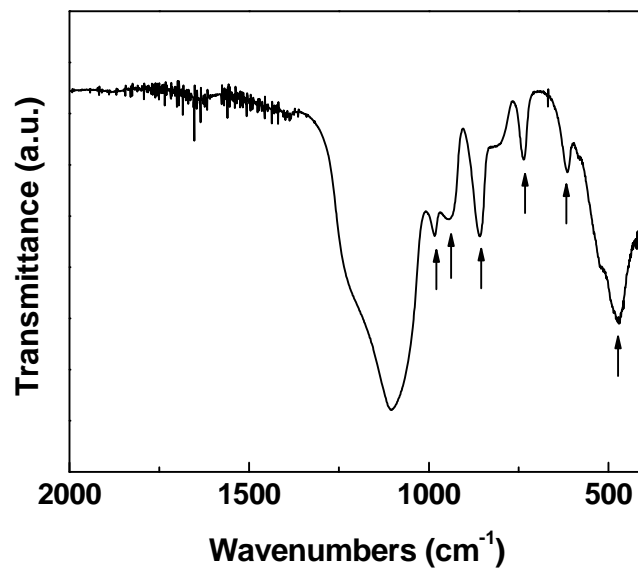
Sample	Li content (mmol·g <sup>-1</sup> )	$S_{\text{BET}}$ (m <sup>2</sup> ·g <sup>-1</sup> )	$V_{\text{p}}$ (cm <sup>3</sup> ·g <sup>-1</sup> )	$D_{\text{p}}$ (nm)	Amount of basic sites (mmol·g <sup>-1</sup> )
SBA-15	0	663	1.13	9.3	0
LiS-1	1.4	458	0.88	8.6	1.5
LiS-2	3.1	404	0.80	8.4	3.2
LiS-3	4.8	336	0.70	8.2	4.9
LiS-4	6.5	279	0.67	7.9	6.3
LiS-5	6.6	277	0.66	7.9	6.4
LiS-r	6.5	9	0.04	–	6.4

<sup>a</sup> Li content was determined by ICP.  $S_{\text{BET}}$ : BET surface area calculated from the adsorption branches;  $V_{\text{p}}$ : total pore volume;  $D_{\text{p}}$ : pore diameter.

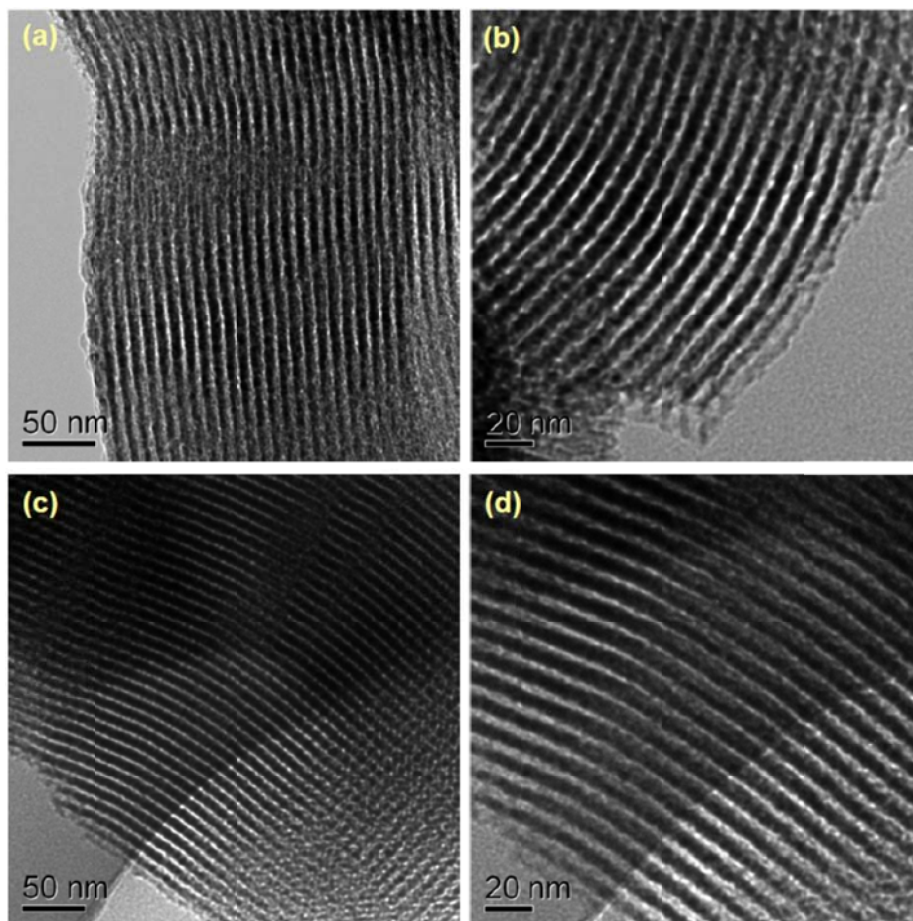
**Table S2. The Yield of DMC under the Catalysis of Various Basic Materials<sup>a</sup>**

Sample	DMC yield (%)			
	0.5 h	1 h	2 h	4 h
MgO	1.3	2.9	4.7	7.6
KL	1.0	2.5	3.0	4.0
CsX	3.0	4.5	5.2	6.1
CaO/SBA-15	2.0	5.4	12.0	13.4
Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	12.5	14.6	17.8	18.8
Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	18.0	22.5	25.1	28.2
CaO/ZrO <sub>2</sub>	7.0	10.1	12.3	15.1

<sup>a</sup>MgO was obtained by calcining the precursor Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at 500 °C for 4 h. The zeolite CsX was prepared by ion exchange of NaX with CsNO<sub>3</sub> for 3 times. The zeolite KL was a commercially available catalyst. CaO/SBA-15 was prepared by impregnation of Ca(NO<sub>3</sub>)<sub>2</sub> into SBA-15 followed by calcination at 550 °C for 2 h. Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> was obtained by impregnation of LiNO<sub>3</sub> into Al<sub>2</sub>O<sub>3</sub> followed by calcination at 600 °C for 2 h. Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> was prepared by impregnation of NaOH into Al<sub>2</sub>O<sub>3</sub> followed by calcination at 600 °C for 2 h. CaO/ZrO<sub>2</sub> was obtained by impregnation of Ca(NO<sub>3</sub>)<sub>2</sub> into ZrO<sub>2</sub> followed by calcination at 550 °C for 2 h.

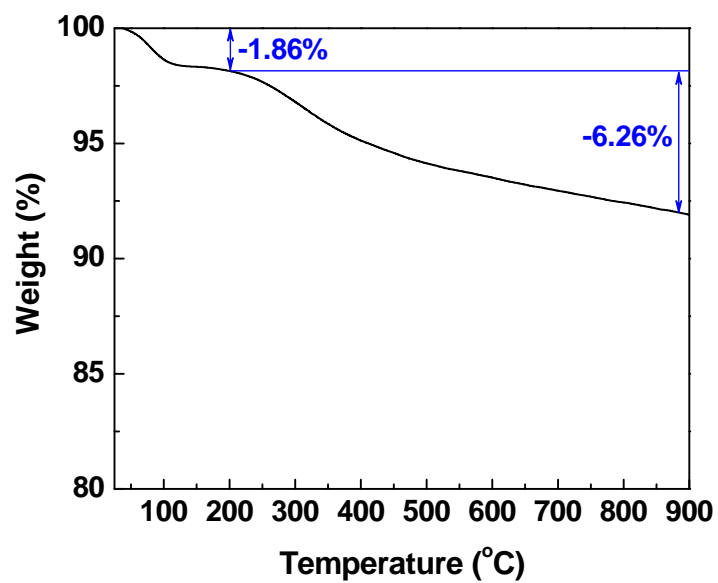


**Figure S1.** IR spectrum of the sample LiS-r. The arrows indicate the bands from  $\text{Li}_2\text{SiO}_3$ .

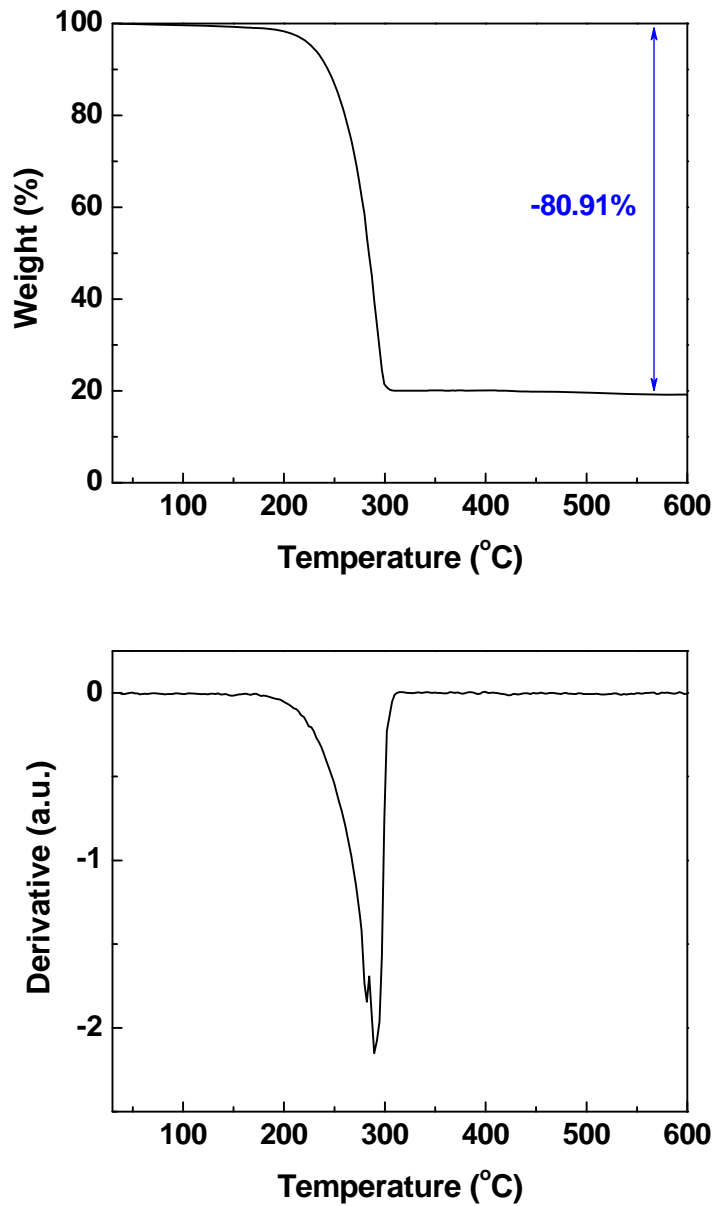


**Figure S2.** TEM images of (a, b) LiS-2 and (c, d) LiS-4 samples at different levels of magnification.

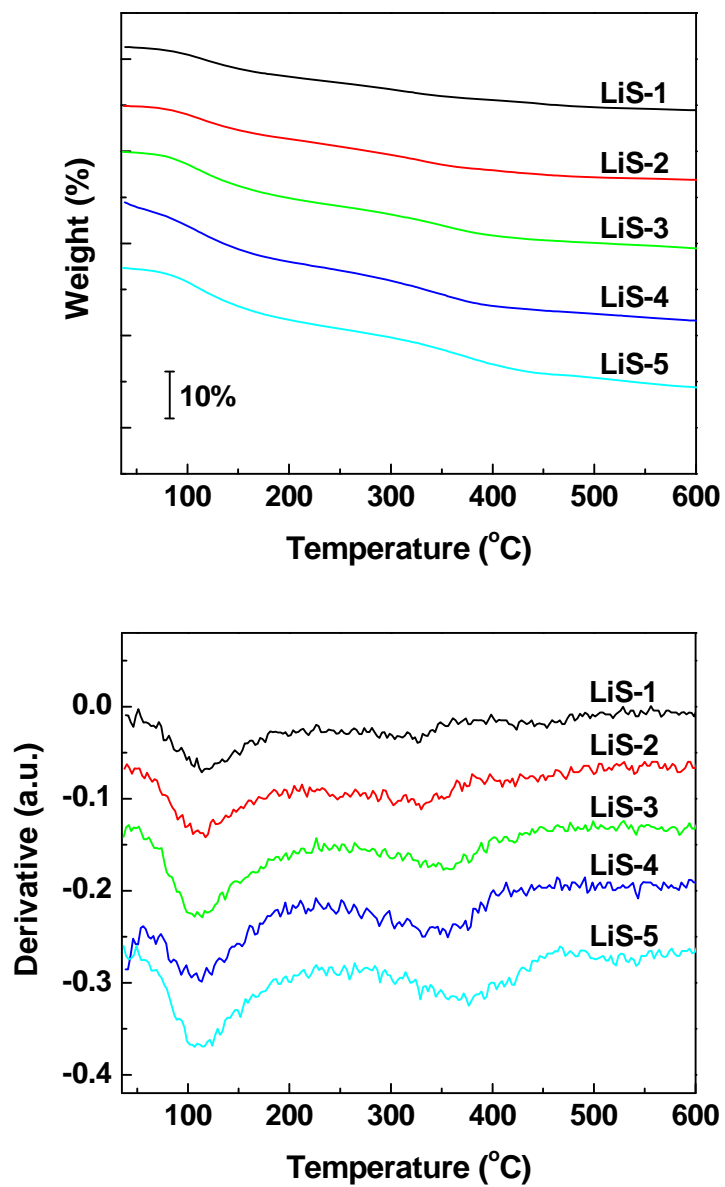




**Figure S3.** TG curve of parent mesoporous silica SBA-15.



**Figure S4.** TG and DTG curve of the pure precursor LTB.



**Figure S5.** TG and DTG curves of LTB-grafted samples. Curves are offset for clarity.