Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supplementary Information

Template-derived carbon: an unexpected promoter for the creation of strong basicity on mesoporous silica

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Experimental section

Materials synthesis

Synthesis of SBA-15. Mesoporous silica SBA-15 was synthesized as follows. In a typical synthesis, 3 g of triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$) was dissolved in 22.5 g of distilled water and 90 g of aqueous HCl solution (2 $mol \cdot L^{-1}$) with stirring at 40 °C. After the formation of homogeneous solution, 6.38 g of tetraethylorthosilicate (TEOS) was added and stirred at this temperature for 24 h. Finally, the resulting gel was transferred to a Teflon-lined autoclave and kept at 100 °C for 24 h under static condition. The precipitate of as-prepared SBA-15 products was filtered off and dried at the room temperature. The content of template in as-prepared SBA-15 is about 50 wt% according to thermogravimetric (TG) analysis. The removal of template was conducted by calcination at 550 °C for 5 h in flowing air.

Carbonization of template. Carbon-containing samples were produced by thermal treatment of as-prepared SBA-15 under a nitrogen atmosphere at different temperatures (300, 500, 700, and 900 °C) for 3 h. The obtained grey samples were denoted as T*x*S, where *x* is the treatment temperature. The grey color was caused by the formation of carbon layers on SBA-15, which is derived from the conversion of template.

Introduction of lithium species. The base precursor, $LiNO_3$, was introduced to the supports by wet impregnation. An identical amount of $LiNO_3$ (20 wt%) was used for all samples. Typically, 0.2 g of $LiNO_3$ was dissolved in 15 mL of deionized water, followed by addition of 0.8 g of support. After stirring at room temperature for 24 h, the mixture was evaporated at 80 °C and subsequently dried at 100 °C for 4 h. This leads to the formation of $LiNO_3$-modified samples, that is $LiNO_3$/SBA-15 and $LiNO_3$/T*x*S, where *x* is the carbonization temperature of template. Aiming to convert $LiNO_3$ to basic sites, $LiNO_3$-modified samples were activated at 400 °C in a N_2 flow for 3 h, leading to the formation of Li_{400}T*x*S when T*x*S were used as supports. In a similar process, $LiNO_3$/SBA-15 was activated at 400 or 600 °C, resulting in the formation of $Li_{400}S$ or $Li_{600}S$, respectively.

Characterization

X-ray diffraction (XRD) patterns of samples were recorded using a Bruker D8 Advance diffractometer with Cu Kα at 40 kV and 40 mA. Nitrogen adsorption-desorption isotherms were measured using an ASAP 2020 system at −196 °C. The samples were degassed at 300 °C for 4 h prior to analysis. The Brunauer-Emmett-Teller (BET) surface area was calculated from the adsorption branch with the relative pressure ranging from 0.04 to 0.20. The pore diameter was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method. Transmission electron microscopy (TEM) images of the materials were captured in a JEM-2010 UHR electron microscope operated at 200 kV. Fourier transform infrared (IR) spectra of the samples diluted with KBr were performed on a Nicolet Nexus 470 spectrometer. The elemental analyses of samples were carried on an Elementar Vario MICRO CUBE (Germany).

To measure the amount of basic sites, 100 mg of sample after activation was added into 10 mL of aqueous HCl. 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 where phenolphthalein was employed as an indicator. The amount of HCl consumed was used to calculate the basicity. Temperature programmed desorption of CO_2 (CO_2-TPD) experiments were conducted on a BELSORP BEL-CAT-A apparatus. The sample was activated at 400 °C (or 600 °C) for 3 h prior to the adsorption of CO_2 at room temperature. After the physical adsorbed CO_2 was purged by a He flow (99.999%) at room temperature, the sample was heated to 800 °C and the CO_2 liberated was detected by a mass spectrometer (HAL201, HIDEN). TG analysis was performed on a thermobalance (STA-499C, NETZSCH). About 10 mg of sample was heated from the room temperature to 800 °C in a flow of N_2. The gaseous products derived from $LiNO_3$ decomposition was also monitored by the mass spectrometer (MS).

Catalytic test

Dimethyl carbonate (DMC) was synthesized from the transesterification of ethylene carbonate and methanol. In a typical process, methanol (0.5 mol, 16 g), ethylene carbonate (0.1

mol, 8.8 g), and catalyst (0.5 wt% of methanol) were added to a three-necked glass flask with a water-cooled condenser. All the catalysts were activated at 400 °C (or 600 °C) in a N_2 flow for 3 h prior to reaction. The reaction was conducted at 65 °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 (GC) equipped with a flame ionization detector (FID).

Additional results and discussion To examine the mechanism for the conversion of $LiNO_3$ with the assistance of carbon, $LiNO_3$ was loaded on pure carbon. The decomposition behavior was studied and the results were shown in Fig. S15. The decomposition of $LiNO_3$ on carbon takes place at about 320 ºC, which is analogous to that on the carbon-coated SBA-15 ($T_{500}S$). Moreover, two main MS signals of m/z = 30 and 44 originated from NO and CO_2 were observed. This suggests an identical pathway for the conversion of $LiNO_3$ supported on carbon.

Table S1 Carbon contents and textual parameters of different samples.

Sample	Carbon content (wt%)	S_{BET} ($m^2 \cdot g^{-1}$)	V_p ($cm^3 \cdot g^{-1}$)	D_p (nm)
SBA-15[a]	0.1	717	1.11	8.1
$T_{300}S$	6.7	797	1.11	9.2
$T_{500}S$	4.0	757	1.01	8.1
$T_{700}S$	3.3	698	1.01	8.1
$T_{900}S$	1.8	618	0.90	7.1

[a] The carbon content of template-containing SBA-15 is 28.3 wt%.

Table S2 Textual parameters of different samples.

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	V_p ($cm^3 \cdot g^{-1}$)	D_p (nm)
$Li_{400}S$	364	0.64	7.1
$Li_{400}T_{300}S$	340	0.58	7.1
$Li_{400}T_{500}S$	305	0.54	7.1
$Li_{400}T_{700}S$	301	0.57	7.1
$Li_{400}T_{900}S$	280	0.62	7.1
$Li_{600}S$	17	0.11	–

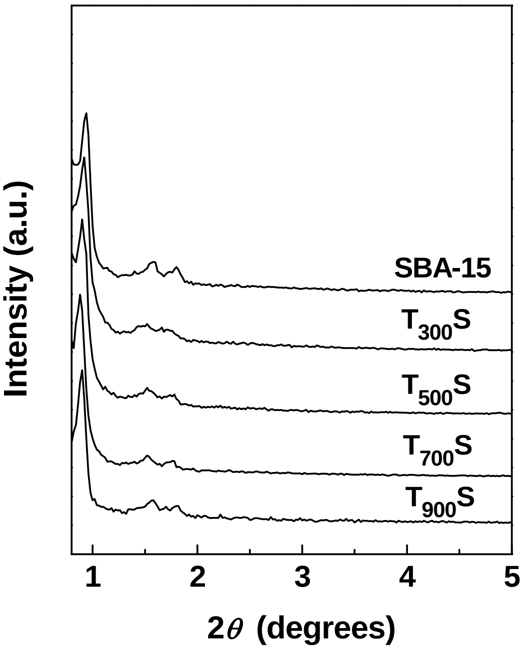

Fig. S1 Low-angle XRD patterns of SBA-15 and template-containing SBA-15 treated at different temperatures.

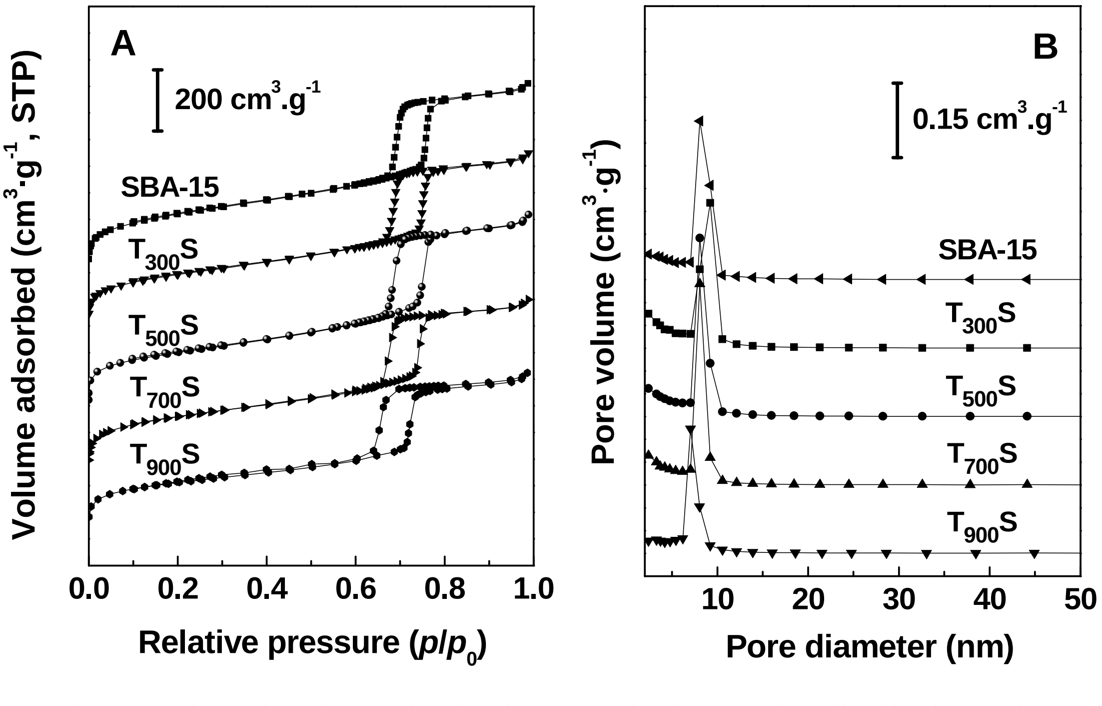

Fig. S2 (A) N_2 adsorption-desorption isotherms and (B) pore size distributions of template-free SBA-15 and template-containing SBA-15 treated at different temperatures. Curves are plotted offset for clarity.

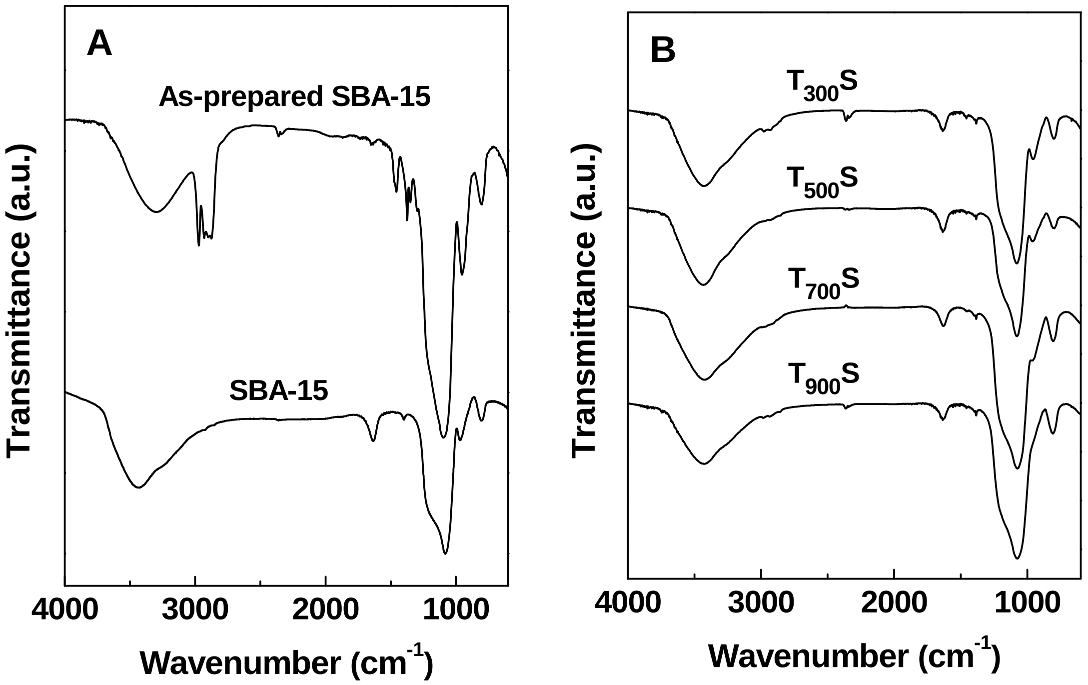

Fig. S3 IR spectra of (A) template-containing and template-free SBA-15 as well as (B) template-containing SBA-15 treated at different temperatures.

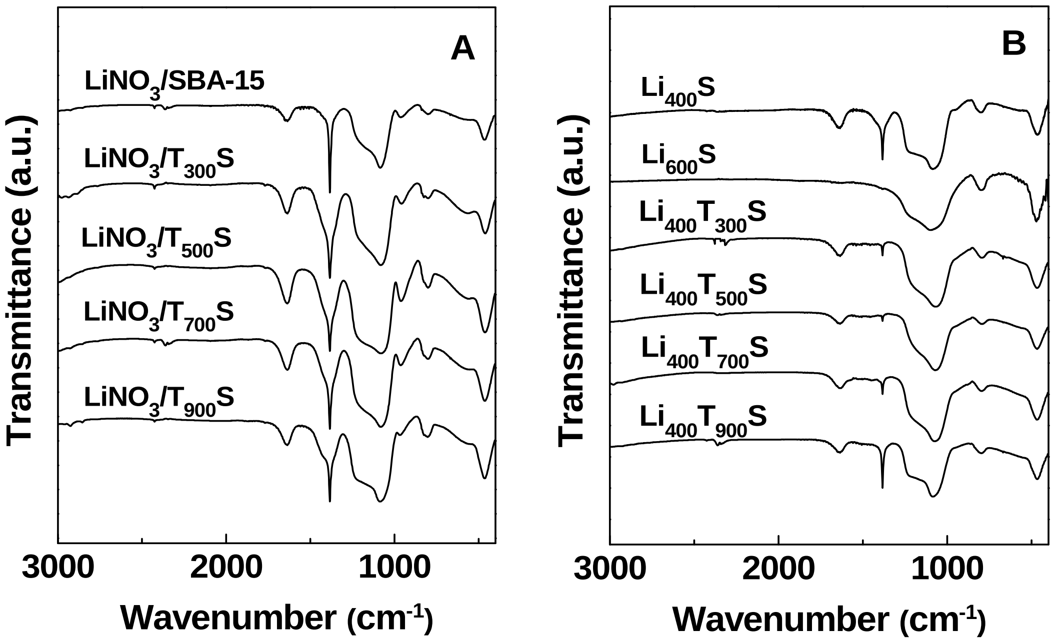

Fig. S4 IR spectra of $LiNO_3$-modified samples (A) before and (B) after activation.

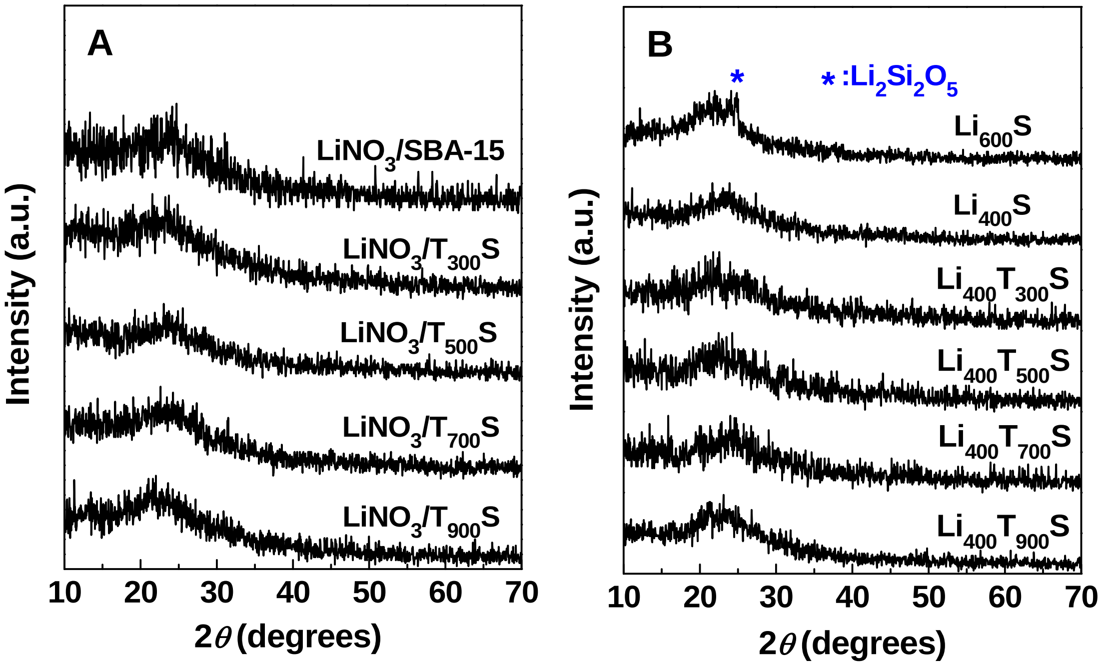

Fig. S5 Wide-angle XRD patterns of LiNO$_3$-modified samples before and after activation.

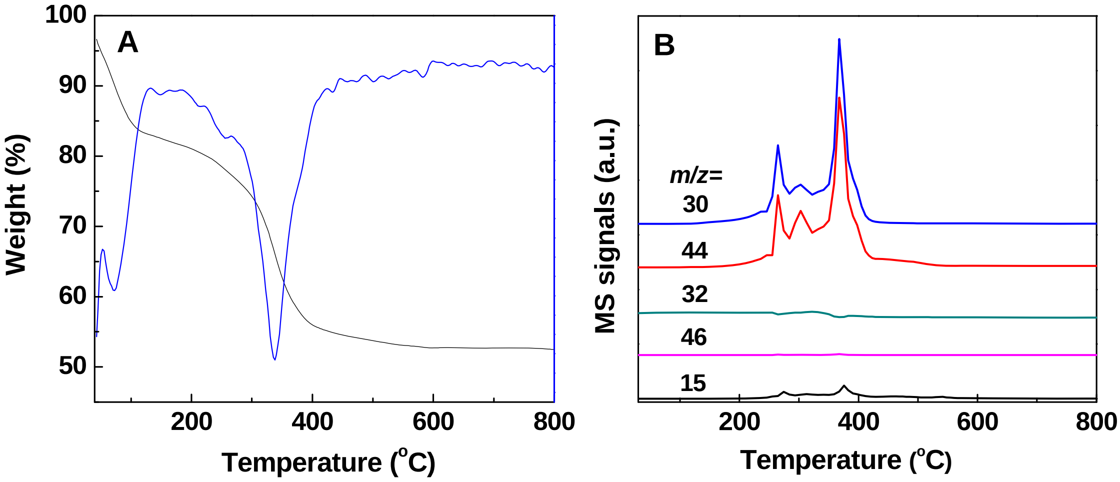

Fig. S6 (A) TG and DTG curves as well as (B) MS signals of gaseous products from the decomposition of LiNO$_3$ supported on T$_{300}$S.

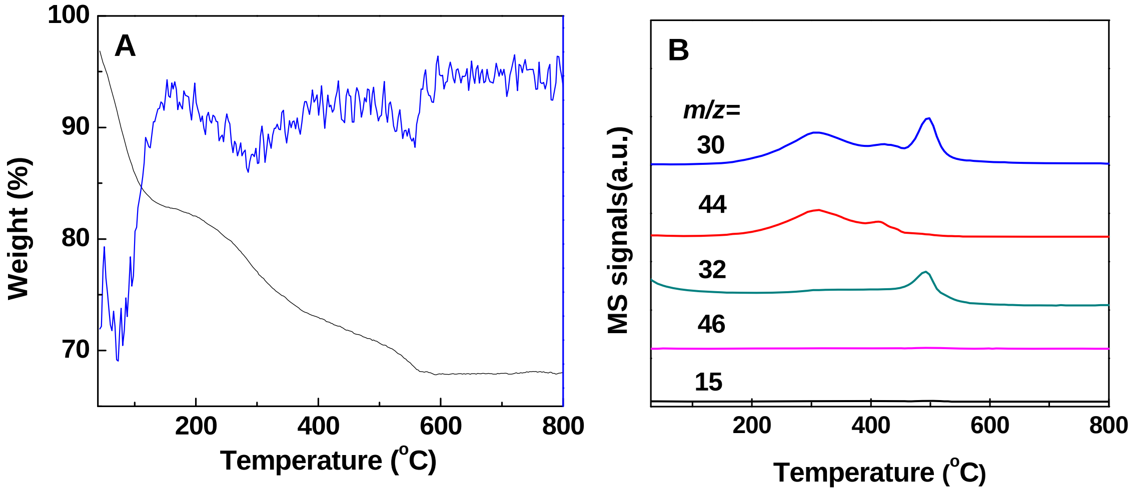

Fig. S7 (A) TG and DTG curves as well as (B) MS signals of gaseous products from the decomposition of $LiNO_3$ supported on $T_{700}S$.

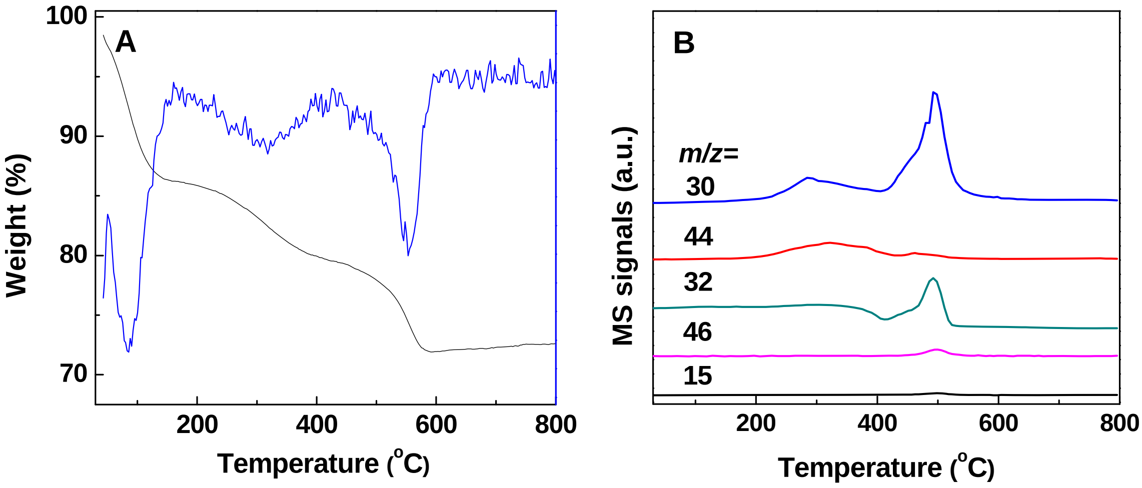

Fig. S8 (A) TG and DTG curves as well as (B) MS signals of gaseous products from the decomposition of $LiNO_3$ supported on $T_{900}S$.

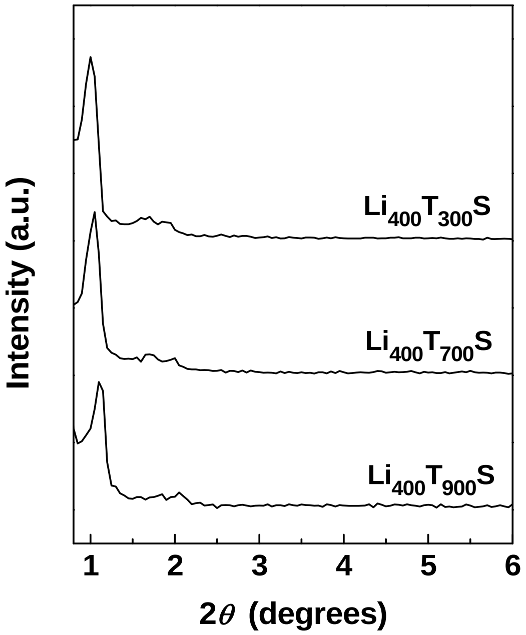

Fig. S9 Low-angle XRD patterns of Li-containing samples.

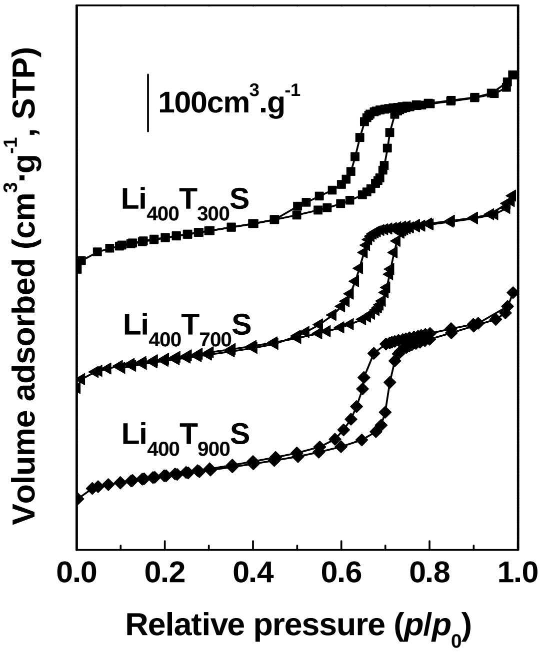

Fig. S10 N_2 adsorption-desorption isotherms of Li-containing samples. Curves are plotted offset for clarity.

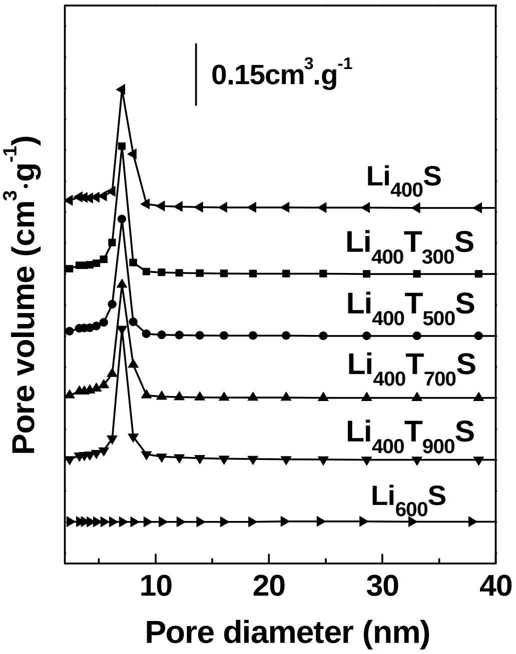

Fig. S11 Pore size distributions of Li-containing samples. Curves are plotted offset for clarity.

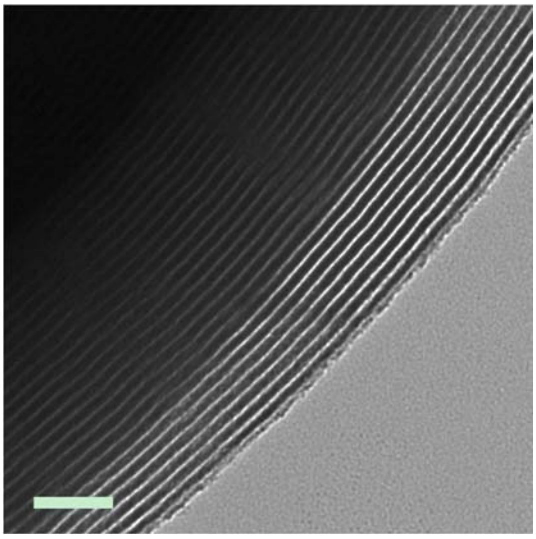

Fig. S12 A TEM image of the sample Li$_{400}$T$_{500}$S. The scale bar represents 50 nm.

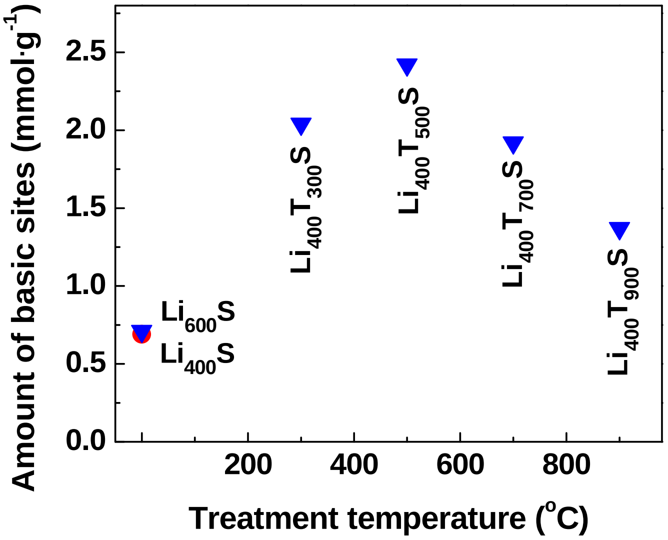

Fig. S13 Amount of basic sites as a function of treatment temperatures used in the carbonization of template.

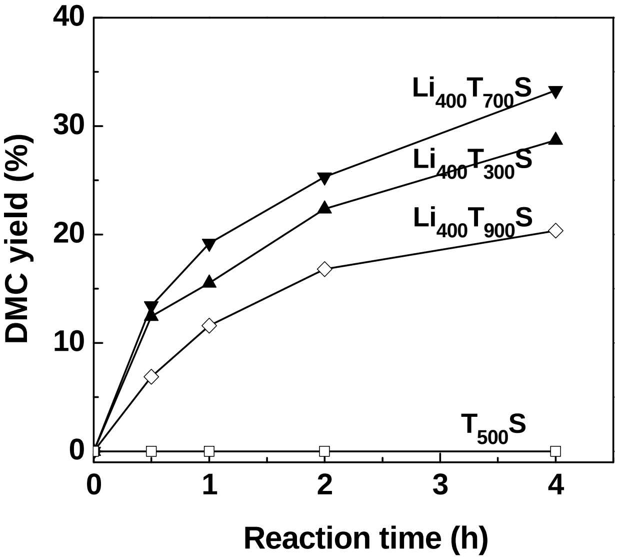

Fig. S14 The yield of DMC under the catalysis of different samples.

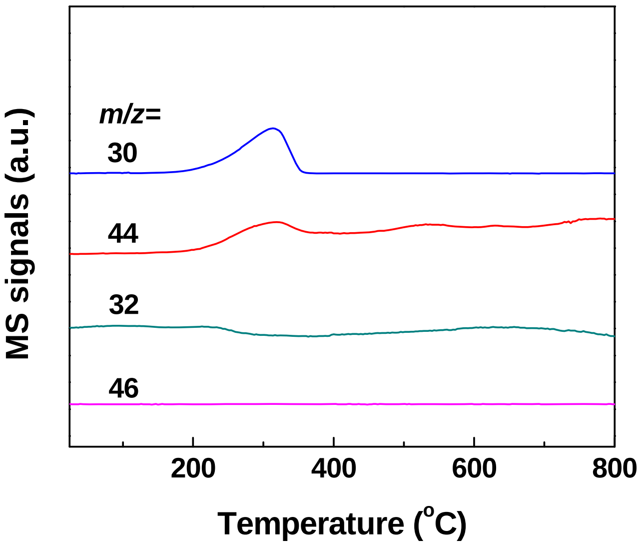

Fig. S15 MS signals of gaseous products from the decomposition of $LiNO_3$ supported on carbon.