

Supporting Information

Low-Temperature Generation of Strong Basicity via an Unprecedented Guest-Host Redox Interaction

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Experimental Section

Materials.

Synthesis of SBA-15. Mesoporous silica SBA-15 was synthesized as follows. Three gram triblock copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was dissolved in 22.5 g distilled water and 90 g aqueous HCl solution (2 M) with stirring at 40 °C. After the formation of homogeneous solution, 6.38 g 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 as-prepared sample was recovered by filtration, washed with water, and air-dried at room temperature. The removal of template was carried out at 550 °C in an air flow for 5 h with a heating ramp of 2 °C·min⁻¹.

Synthesis of CS. Furfuryl alcohol (FA) and oxalic acid were used as the carbon precursor and polymerization catalyst, respectively, and were introduced to SBA-15 by impregnation. After evaporation of the solvent ethanol, the resulting solid were polymerized at 80 °C for 2 h under air. Afterwards, the composite was heated at 150 °C for 3 h and then evacuated for 1 h in order to remove unreacted FA. Carbonization was carried out at 700 °C for 3 h with a heating rate of 3 °C·min⁻¹. The heating furnace was purged with an N₂ flow during the carbonization process until the sample was cooled to room temperature. The starting composition was 1 g SBA-15: x g FA: 0.1 x g oxalic acid: 5 g ethanol ($x = 0.1, 0.2, 0.4,$ and 0.8). The resultant carbon-coated SBA-15 samples were denoted as CS- m , where m is 1, 2, 3, or 4 and corresponds to the content of FA is 0.1, 0.2, 0.4, and 0.8 g per gram SBA-15.

Synthesis of KCS and KS. The base precursor, KNO₃, was introduced to supports by wet impregnation. An identical amount of KNO₃ (20 wt%) was used for all samples. Typically, 0.2 g KNO₃ was dissolved in 15 mL deionized water, followed by addition of 0.8 g 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. The obtained solid was calcined at 400 °C in a N₂ flow for 3 h to convert KNO₃, leading to the formation of KCS- m if CS- m were used as supports. In a similar process, KNO₃ was directly introduced to SBA-15 and calcined at 400 and 600 °C,

and the resultant samples were denoted as KS(400) and KS(600), respectively.

Characterization.

X-ray diffraction (XRD) patterns of samples were recorded using a Bruker D8 Advance diffractometer with Cu K α 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 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.

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 CO₂ (CO₂-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 CO₂ at room temperature. After the physical adsorbed CO₂ was purged by a He flow (99.999%) at room temperature, the sample was heated to 800 °C and the CO₂ liberated was detected by a mass spectrometer (HAL201, HIDEN). Thermogravimetric (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 N₂ (for the conversion of supported KNO₃) or air (for the analysis of carbon contents). The gaseous products derived from KNO₃ decomposition was also monitored by the mass spectrometer.

Catalytic test.

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

(0.1 mol), 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 N₂ flow (99.999%) 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 equipped with a flame ionization detector.

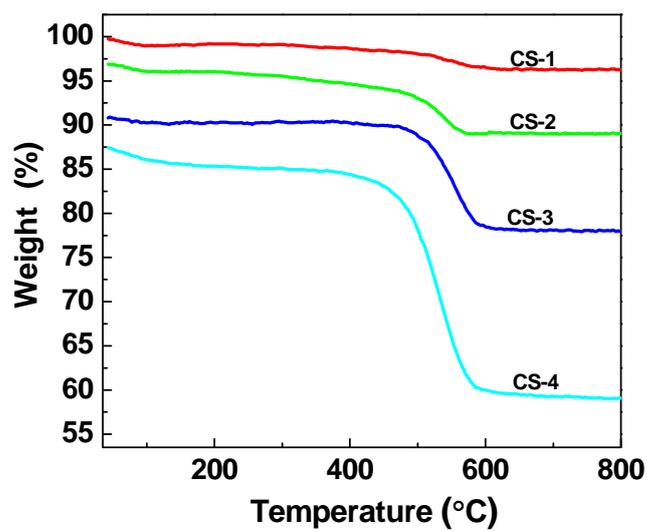


Figure S1. TG curves of CS samples in an air flow.

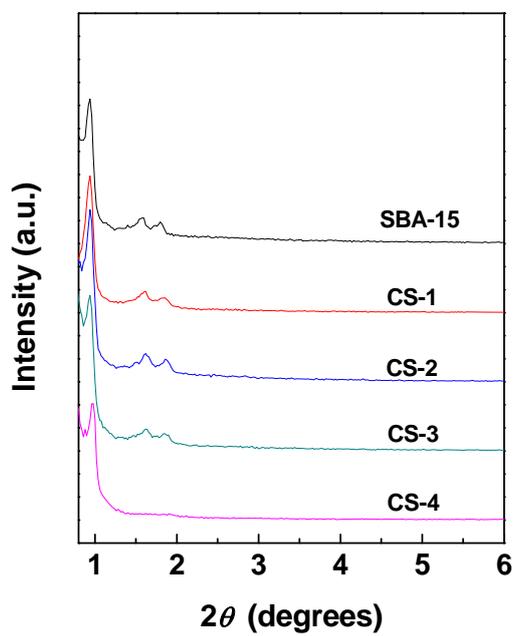


Figure S2. Low-angle XRD patterns of parent SBA-15 and CS samples.

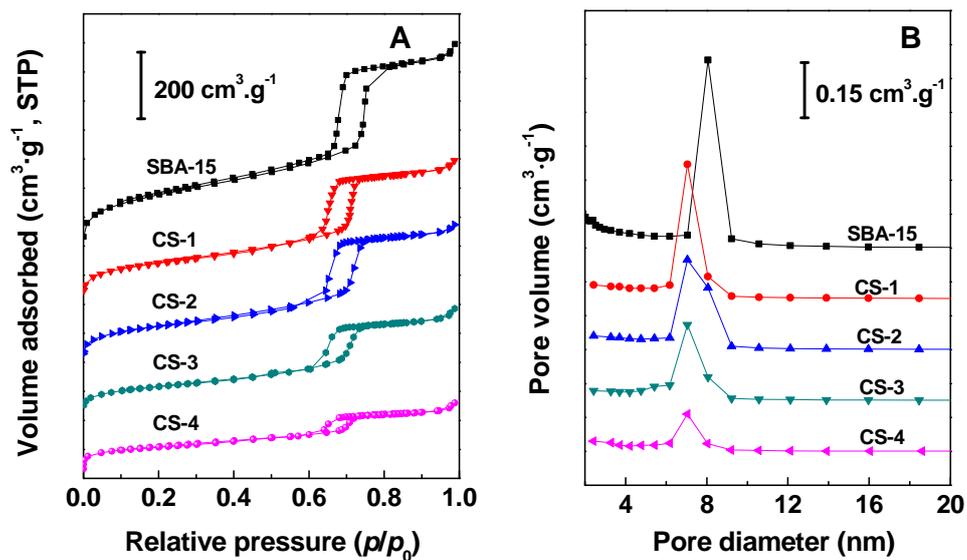


Figure S3. (A) N₂ adsorption-desorption isotherms and (B) pore size distributions of SBA-15 and CS samples.

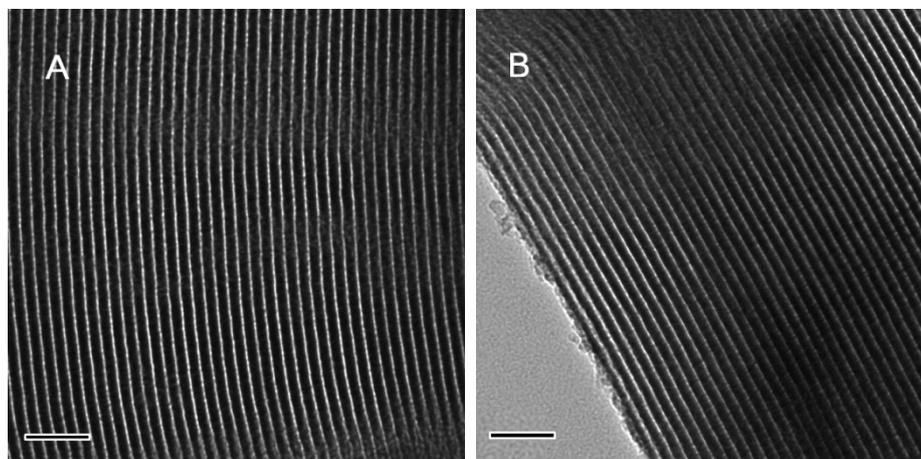


Figure S4. TEM images of (A) CS-3 and (B) KCS-3. Scale bars represent 50 nm.

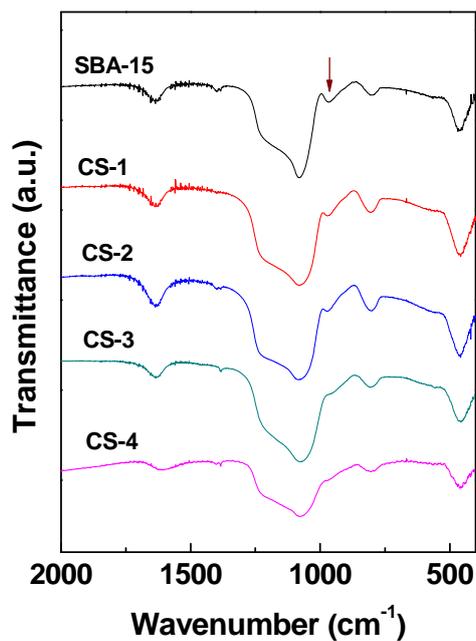


Figure S5. IR spectra of SBA-15 and CS samples.

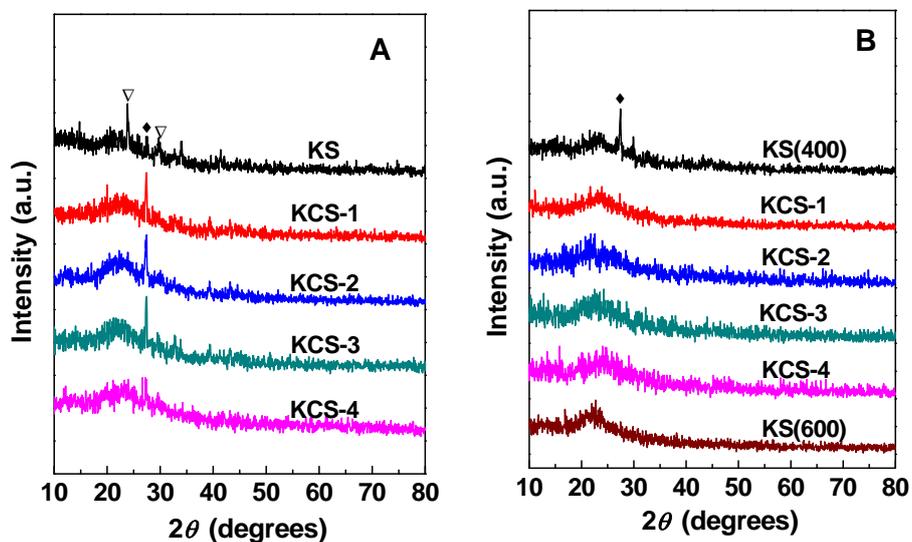


Figure S6. Wide-angle XRD patterns of KS and KCS samples (A) before and (B) after activation at 600 °C for KS(600) and 400 °C for other samples. ▽ and ◆ denote KNO₃ of orthorhombic and hexagonal phases, respectively.

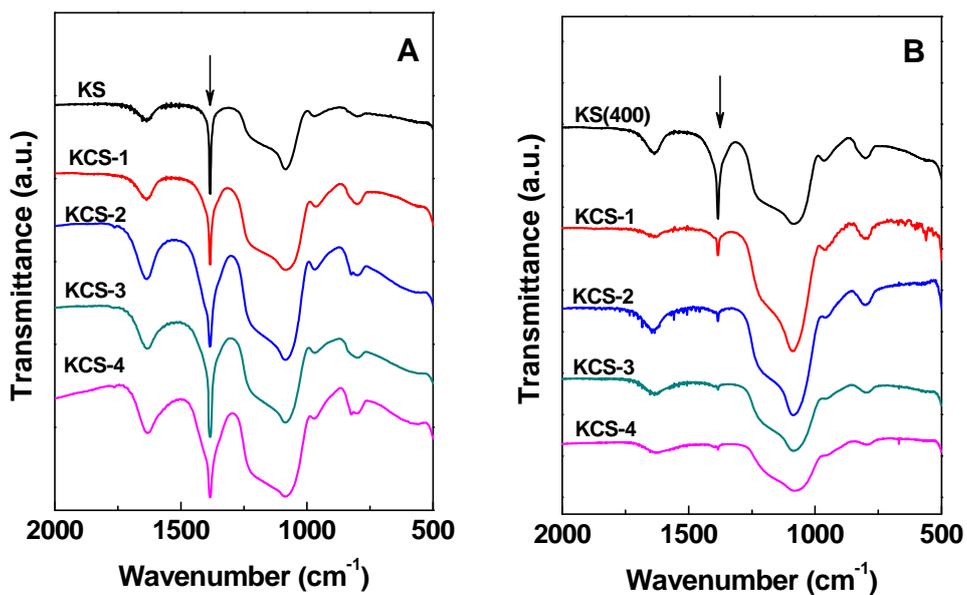


Figure S7. IR spectra of KS and KCS samples (A) before and (B) after activation at 400 °C.

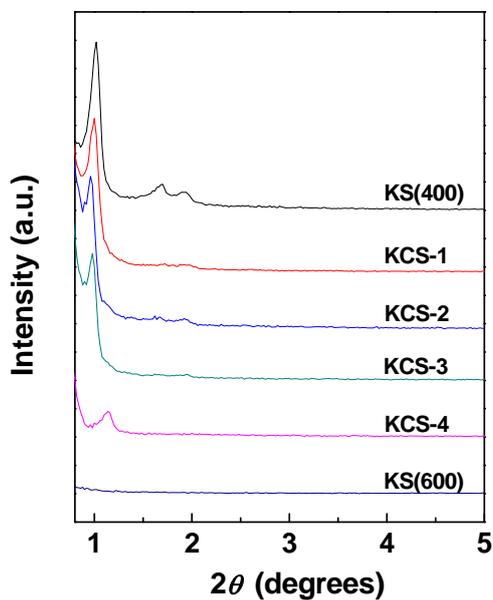


Figure S8. Low-angle XRD patterns of KS(400), KS(600), and KCS samples.

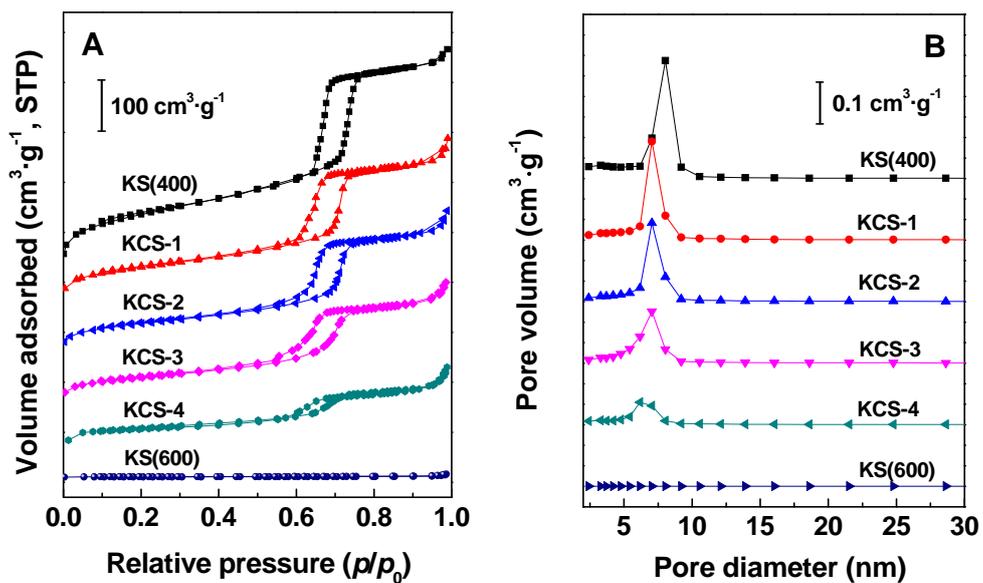


Figure S9. (A) N₂ adsorption-desorption isotherms and (B) pore size distributions of KS(400), KS(600), and KCS samples.

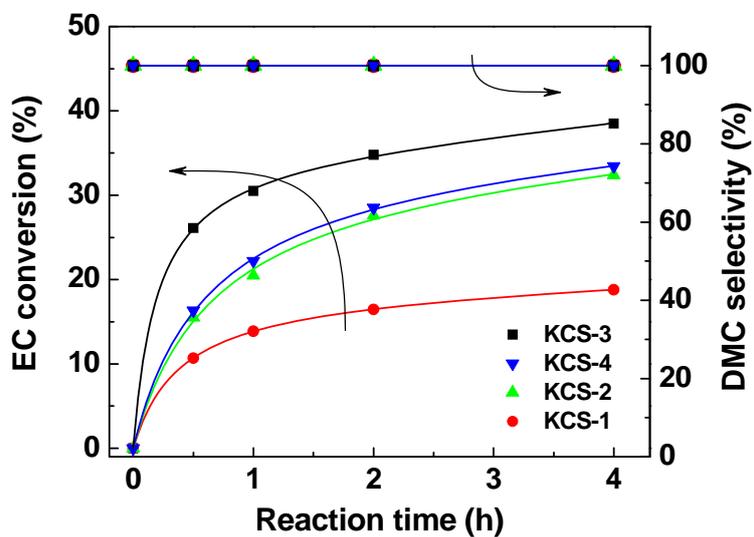


Figure S10. The conversion of EC and the yield of DMC under the catalysis of KCS samples.

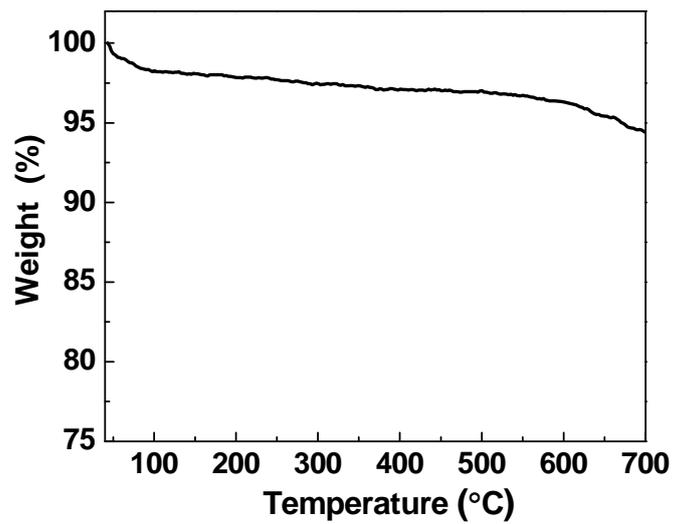


Figure S11. TG curve of CS-3 in a nitrogen flow.