SUPPORTING INFORMTAION

Silicon Oxynitrides of KCC-1, SBA-15 and MCM-41 for CO_2 Capture with Excellent Stability and Regenerability

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EXPERIMENTAL SECTION

1. Synthesis of KCC-1, SBA-15 and MCM-41. KCC-1, SBA-15 and MCM-41 were synthesized following a previously reported procedure via the template-mediated hydrolysis-polycondensation of tetraethyl orthosilcate (TEOS). In the case of KCC-1, TEOS (2.5 g) was dissolved in a solution of cyclohexane (30 mL) and pentanol (1.5 mL). A stirred solution of cetylpyridinium bromide (CPB) (0.5 g) and urea (0.6 g) in water (30 mL) was then added. This mixture was stirred for 30 min at room temperature and was then exposed to microwaves at 120 °C for 2.5 h. The product was washed with water and air dried. The template was removed by calcination at 550 °C for 6 h in a continuous flow of air, and the obtained material is designated as KCC-1.

In the case of SBA-15, tri-block poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) $[(EO)_{20}(PO)_{70}(EO)_{20}]$ (4 g) was dissolved in a mixture of water (30 mL) and hydrochloric acid (2 M, 120 mL) and stirred for 30 min at 40 °C. TEOS (9.15 mL) was then added, and the solution was further stirred for 24 h. This mixture was then autoclaved at 100 °C for 24 h. The product formed was washed with water and dried at 80 °C for 24 h. The template was removed by calcination at 550 °C for 6 h in a continuous flow of air, and the obtained material is designated as SBA-15.

In the case of MCM-41, cetyltrimethyl ammonium bromide (CTAB) (8.8 g) was dissolved in a mixture of water (208 mL) and aqueous ammonia (96 mL, 35 %) at 35 °C. To this solution, TEOS (40 mL) was added slowly under stirring. After further stirring for 3 h, the gel formed was aged in a closed container at room temperature for 24 h. The product was washed with water and air dried. The template was removed by calcination at 550 °C for 6 h in a continuous flow of air, and the obtained material is designated as MCM-41.

2. Amino-Functionalization by Nitridation. The amino-functionalization of these materials was achieved via thermal ammonolysis (nitridation) using a flow of ammonia gas. Nitridation was performed using a plug-flow fixed-bed metal reactor (inner diameter of 5 mm) placed vertically inside the tubular furnace. Typically, 200-300 mg of material (KCC-1, SBA-15 or MCM-41) was loaded in the reactor with a 100 mL/min flow of argon, and the furnace was heated to 100 °C at a ramp rate of 5 °C/min. The flow was changed to pure ammonia gas and held for 10 h at the desired temperature (400, 500, 600, 700, 800 or 900 °C). The furnace was cooled to 100 °C, the gas flow was changed to 100 mL/min of argon, and the furnace was further cooled to room temperature. The nitrided samples were designated as KCC-1-N, SBA-15-N and MCM-41-N followed by the nitridation temperature.

3. Organic Amine Grafting: Grafting of APTES was achieved by refluxing 0.5 g of calcined KCC-1, SBA-15 or MCM-41 with (3-aminopropyl)triethoxysilane (5 mL) in 50 mL of toluene for 24 h. The resulting material was washed repeatedly with toluene and then dried under vacuum at 60 °C for 12 h. The obtained samples were designated as KCC-1-APTES, SBA-15-APTES, MCM-41-APTES.

Table S1. Physicochemical properties, nitrogen contents and CO_2 adsorption capacity of solvent extracted-nitridated materials.

Sample ID	BET Surface Area ($m^2 g^{-1}$)	Average Pore Diameter (nm)	BJH Pore Volumes ($cm^3 g^{-1}$)	Nitrogen Content (wt. %)	CO_2 Adsorption Capacity (mmol g^{-1})
KCC-1-Series					
KCC-1-Sol	397	7.31	0.78	Not detected	0.19
KCC-1-Sol-N400	361	7.28	0.73	0.55	0.27
KCC-1-Sol-N500	349	7.21	0.61	0.53	0.31
KCC-1-Sol-N600	351	7.24	0.57	0.90	0.48
KCC-1-Sol-N700	328	7.18	0.41	4.32	1.07
KCC-1-Sol-N800	331	7.03	0.32	12.75	1.18
KCC-1-Sol-N900	304	6.94	0.23	21.05	1.12
SBA-15-Series					
SBA-15-Sol	602	7.15	0.83	0.01	0.76
SBA-15-Sol-N400	590	7.02	0.78	0.07	0.88
SBA-15-Sol-N500	568	6.95	0.71	0.54	1.28
SBA-15-Sol-N600	547	6.84	0.63	0.84	1.93
SBA-15-Sol-N700	519	6.69	0.52	4.87	2.22
SBA-15-Sol-N800	461	6.31	0.41	7.89	2.02
SBA-15-Sol-N900	403	6.08	0.29	14.76	2.12
MCM-41-Series					
MCM-41-Sol	490	1.97	1.23	1.06	1.25
MCM-41-Sol-N400	483	1.95	1.19	0.53	1.12
MCM-41-Sol-N500	470	1.86	1.13	0.7	1.70
MCM-41-Sol-N600	458	1.72	1.12	1.64	2.20
MCM-41-Sol-N700	447	1.66	1.03	8.38	2.72
MCM-41-Sol-N800	438	1.54	0.92	13.67	2.18
MCM-41-Sol-N900	430	1.37	0.88	22.45	2.29

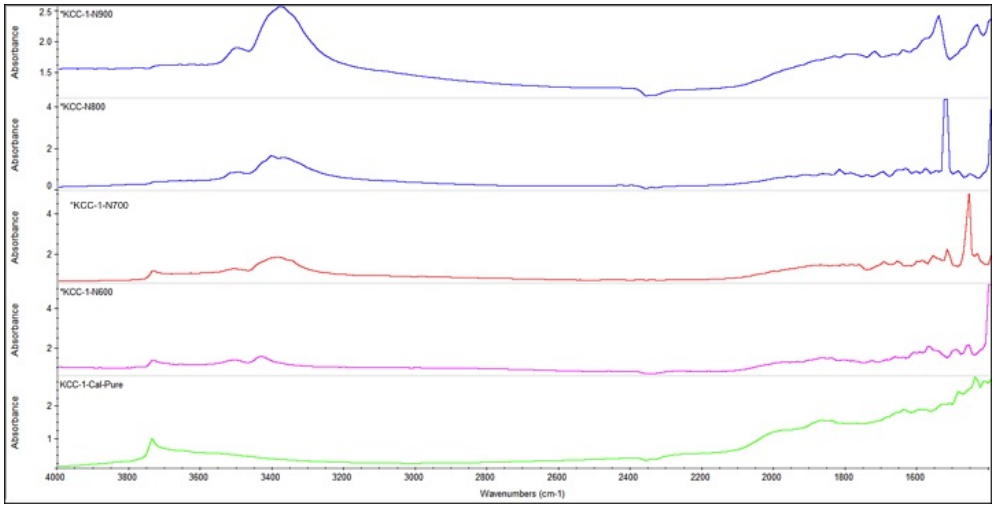

Figure S1. IR of KCC-1 Series

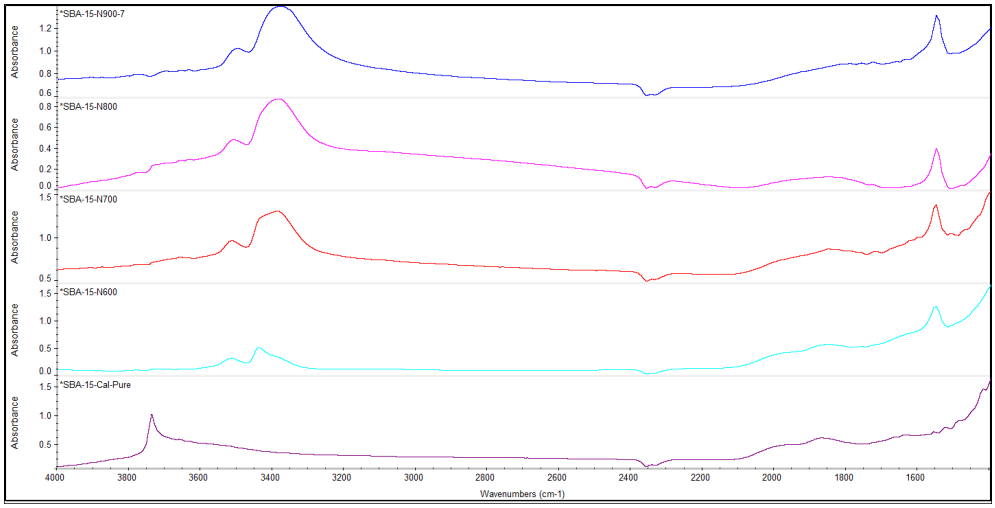

Figure S2. IR of SBA-15 Series

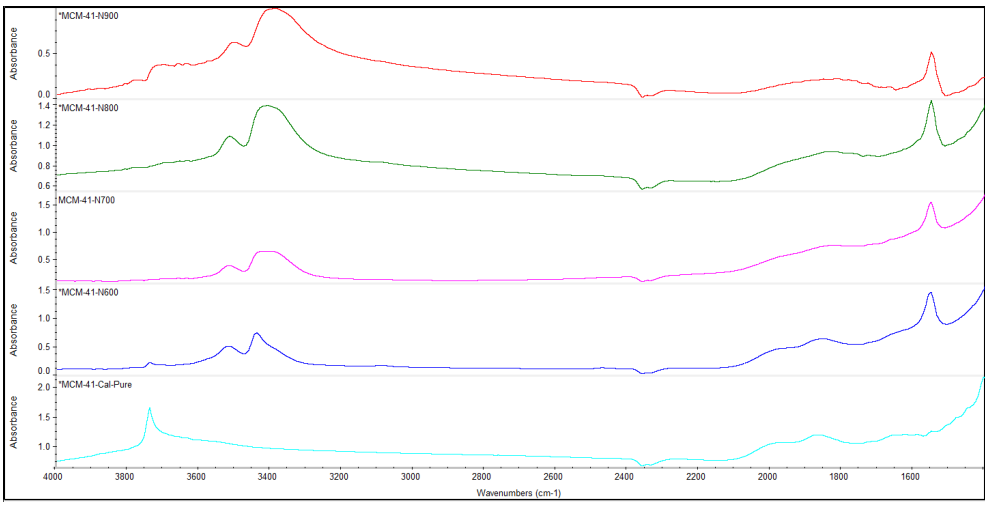

Figure S3. IR of MCM-41 Series

^{29}Si-MAS-NMR Spectroscopic Analysis of the As-Synthesized Materials: All NMR experiments were conducted using a WB AVANCE III 600 MHz NMR spectrometer. The ^{29}Si MAS NMR spectra (Figure S1,S2,S3) were recorded at a resonance frequency of 119.23 MHz with 20 kHz pining rate using a Broadband BB/1H 3.2 mm Bruker CP/MAS probe. The temperature for all experiments was maintained at 298 K. Each spectrum was induced by a nonselective one pulse using standard one pulseeq program from bruker pulse library. To achieve a sufficient signal-to-noise ratio, 2k transients were collected with 30 s recycle delay. Exponential line broadening of 10 Hz applied before Fourier Transformation and Bruker Topspin 3.0 software was used for data collection and for spectral analysis.

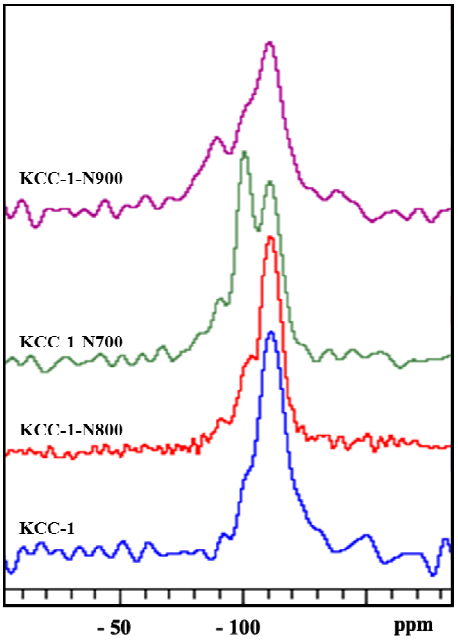

Figure S4. ^{29}Si-MAS-NMR of KCC-1 Series

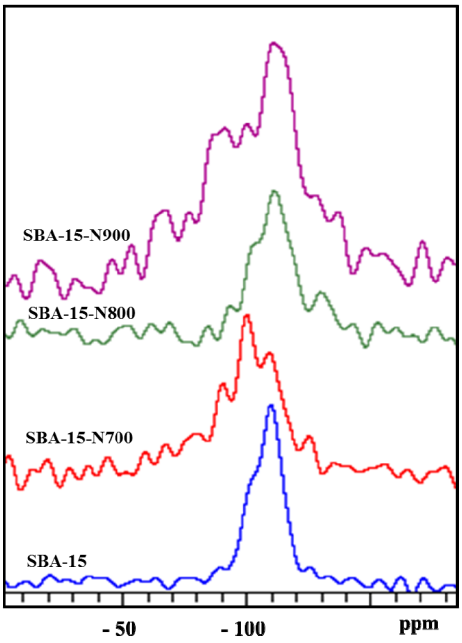

Figure S5. ^{29}Si-MAS-NMR of SBA-15 Series

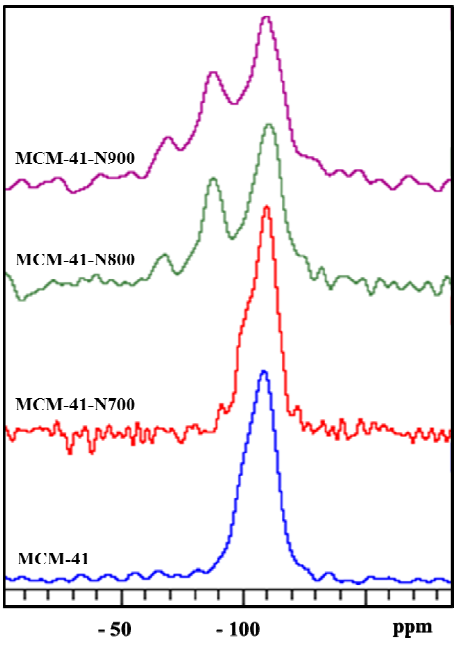

Figure S6. ^{29}Si-MAS-NMR of MCM-41 Series

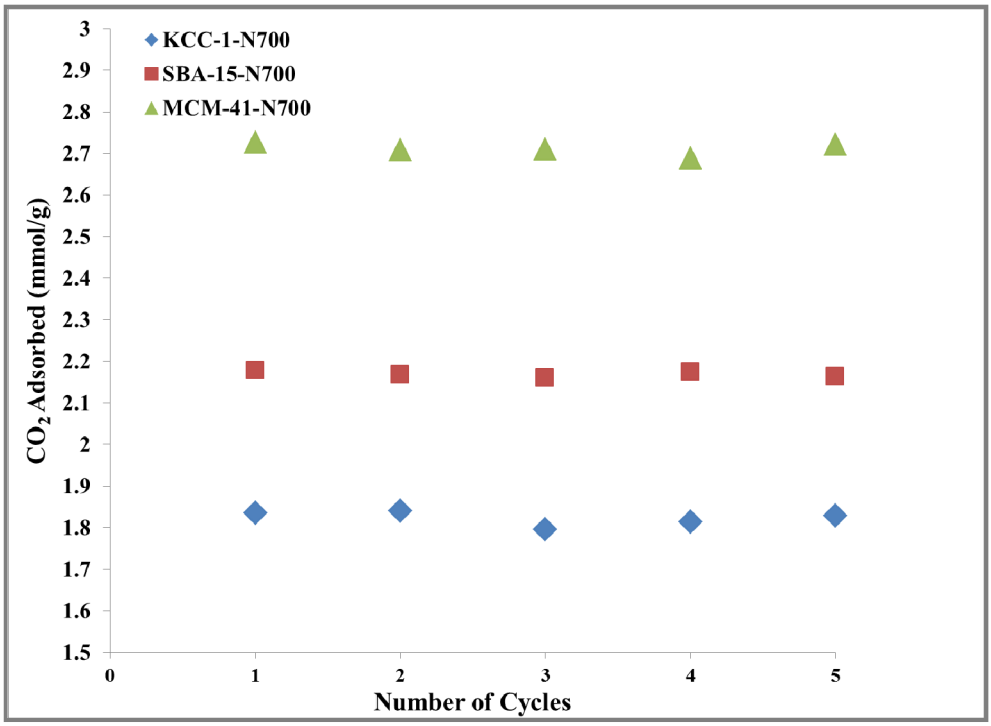

Figure S7. Regeneration and reuse of sorbents: KCC-1-N700, SBA-15-N700 and MCM-41-N700

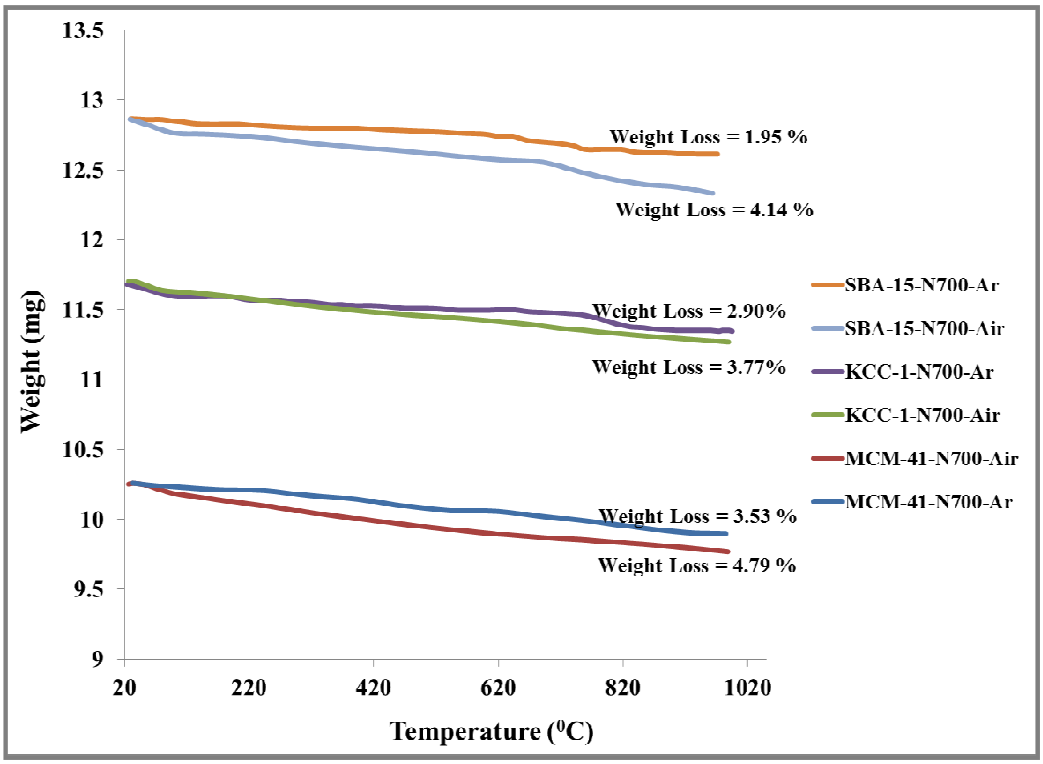

Figure S8. Thermal gravimetric analysis of sorbents in air and in argon.