Supporting Information

Microwave-assisted synthesized SAPO-56 as catalyst in the conversion of CO_2 to cyclic carbonates

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Synthesis of SAPO-56 crystals via conventional hydrothermal synthesis

SAPO-56 crystals were synthesized hydrothermally following the synthetic procedure reported by Wilson *et al*. (*Microporous and Mesoporous Materials* 1999, 28, 125). In a typical synthesis a solution of orthophosphoric acid (85 wt.%, Sigma-Aldrich) deionized water, and aluminium hydroxide (76.5% min, Alfa Aesar) was vigorously stirred for ~1 hr. To this solution, Ludox AS-40 colloidal silica (40 wt.%, Sigma-Aldrich) and N,N,N',N'-tetramethyl-hexane-1,6-diamine (TMHD, Aldrich) were added. The resultant solution was stirred for 24 hours at room temperature. The gel composition was: 2.0 TMHD: 0.6 SiO_2: 0.8 Al_2O_3: P_2O_5: 40 H_2O. The resultant gel was transferred to into a stainless-steel autoclave and heated up to 200°C for 96 hr. Then, the autoclave was cooled down and the solid product was recovered by centrifugation, washed three times with deionized water and dried at 100°C overnight. Calcination was carried out at 400°C for 20 h with heating rate of 1°C/min and cooling rate of 5°C/min to remove the organic template.

Characterization techniques

The morphology of the crystals was determined with a FE-SEM (FEI Nova 600) with an acceleration voltage of 6 kV. Powder X-ray diffraction patterns were collected using a Bruker D8-Discover diffractometer at 40 kV, 40 mA with Cu Kα radiation. Transmission electron microscopy (TEM) studies, including TEM imaging, selected area electron diffraction (SAED), and energy-dispersive x-ray spectroscopy (EDS), were performed using a FEI Tecnai F20 transmission electron microscope. A field emission gun (FEG) was used for the electron source and the studies were performed at the accelerating voltage of 200 keV. Carbon dioxide adsorption isotherms were collected using a Micromeritics Tristar 3000 porosimeter at room temperature employing water as coolant. Prior to the measurements, the samples were degassed at 150°C for ~3h.

The acidic properties of the MW SAPO-56 was determined using NH_3 as a probe molecules. In temperature-programmed desorption of ammonia (NH_3-TPD; Micromeritics Auto Chem 2910 instrument), 0.1 g of the catalyst was taken in a U-shaped, flow-through, quartz sample tube. Prior to measurements, the catalyst was pretreated in He (30 ml/min) at 250 °C for 1 h. A mixture of NH_3 in He (10 vol%) was passed (30 ml/min) at 50 °C for 1 h. The sample was, then, flushed with He (30 ml/min) for 1 h. TPD measurements were carried out by raising the temperature from 100 to 500 °C at a heating rate of 5 °C/min. From the areas of the desorption peaks and from the calibration curves generated prior to the analyses of the catalyst samples, the amount of acid sites present in the catalysts were determined.

The solid-state NMR spectra were recorded at room temperature and ambient pressure on a Tecmag Discovery spectrometer using a Doty Scientific magic angle-spinning (MAS) probe with 7 mm (outside diameter) sapphire rotors.

Cross-polarization with MAS (CP-MAS) was used to acquire 29Si data at 59.622 MHz. The 1H ninety-degree pulse width was 3.7 μs. The mixing time was 1.5 ms. The MAS sample spinning rate was 2.5 kHz or 4 kHz. Recycle delay between scans was 2 s with the acquisition time to be 20.48ms, determined by observing no apparent loss in the 29Si signal from one scan to the next. The 29Si chemical shifts are given relative to hexamethylcyclotrisiloxane ($[(CH_3)_2SiO]_3$) as secondary reference, which has a chemical shift to be 9 ppm calibrated using the 29Si signal of TMS assigned to zero ppm.

For one pulse experiments, the 29Si data were also acquired at 59.622 MHz. The 29Si pulse width was 1.5 μs, and the delay time was 30 s. The spinning rate of the rotors was either 2.5 kHz or 3.0 kHz, depending upon the stability of the rotation. All the other parameters were the same as CPMAS experiments.

Catalytic activity

The catalytic activity of SAPO-56 was evaluated in the cycloaddition of CO_2 to epichlorohydrin to form chloropropene carbonate. In a typical cycloaddition reaction, 18 mmol of epichlorohydrin and 100 mg of SAPO-56 were placed in a 250 ml stainless steel high pressure Parr reactor (Model 4576A). The reactor was pressurized with CO_2 at 10 bar, and the reaction was carried out at different temperatures for 4h (100°C was chosen as the temperature for MW heated and hydrothermal samples, because it was the optimum temperature for higher yields to chloropropene carbonate for hydrothermal synthesized samples (see Figure A1). After the reaction, the reactor was cooled to room temperature, the unreacted CO_2 was vented out, the catalyst was separated by centrifugation, and the products were analyzed by ^1H NMR spectrometry (Varian 7600 AS 400 MHz). The yield to chloropropene carbonate was calculated by using ^1H NMR spectra, from signs obtained at chemical shifts of 4.54ppm (^1H from chloropropene carbonate), 3.17ppm (^1H from epichlorohydrin) and 3.9 (^1H from the by-product 3-chloro-1,2-propanediol). GC-MS (HP 5890 Gas Chromatograph equipped with 5970 Mass Selective Detector; 30m X 0.32 mm column, HP-5 coated with 5% phenyl methyl poly siloxane stationary phase) was employed to confirm the presence of chloropropene carbonate, epichlorohydrin, and diol.

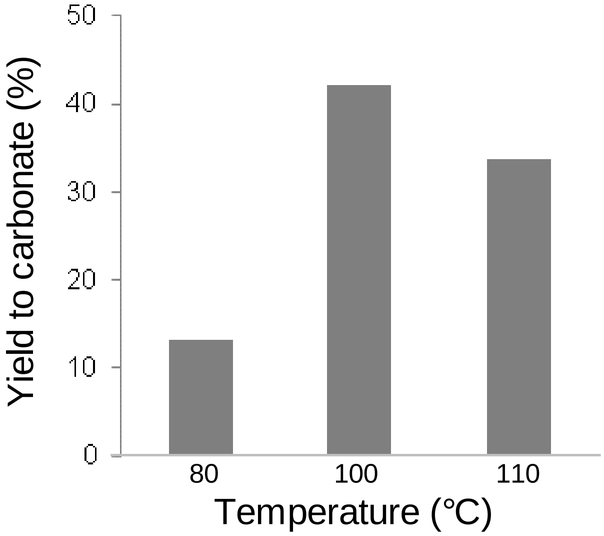


Figure A1. Yield to chloropropene carbonate as a function of temperature for hydrothermal synthesized SAPO-56. The optimum temperature (100 °C) was chosen to test the catalytic activity of the MW sample.

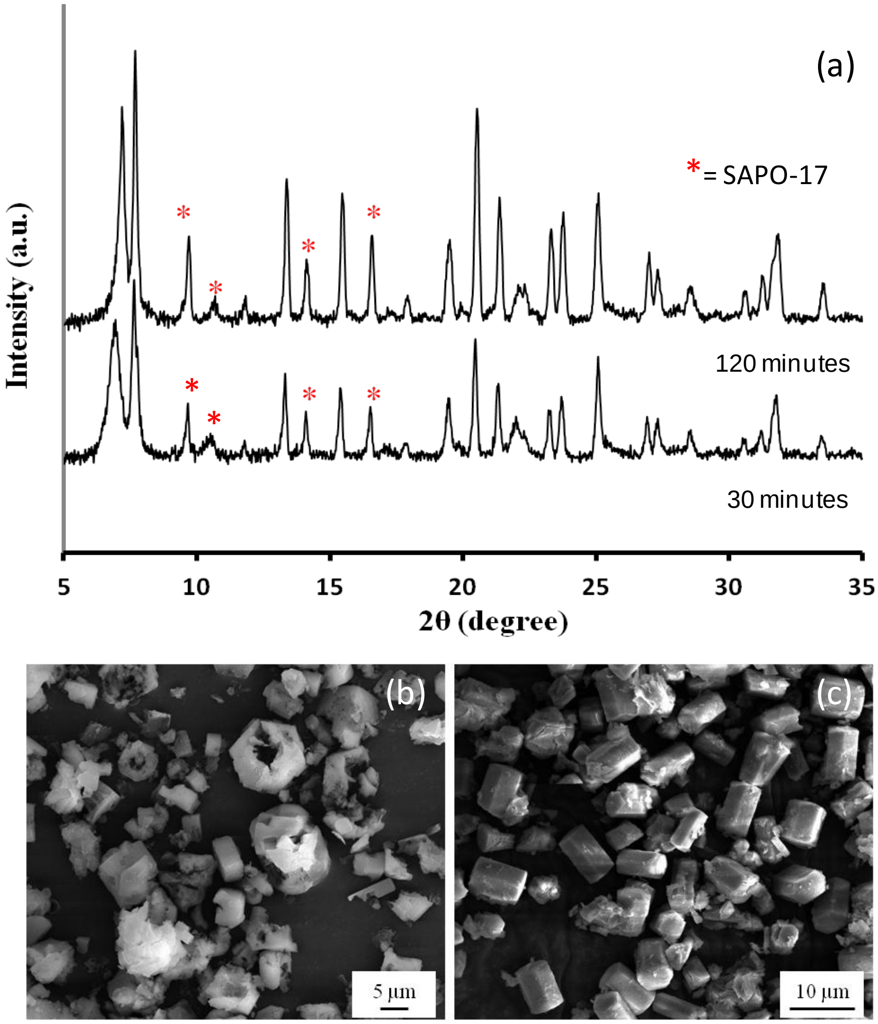
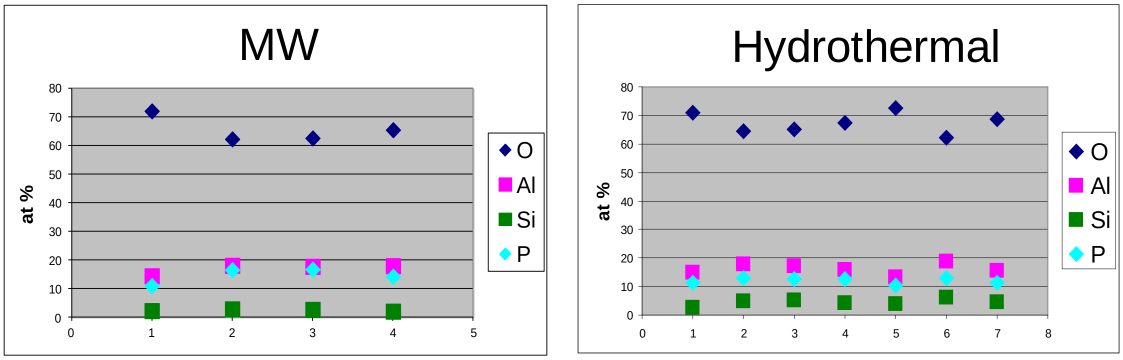


Figure S1. (a) XRD patterns of MW heated synthesized SAPO-56 crystals at 30 minutes and 120 minutes. Representative SEM images of the sample synthesized at (b) 30 minutes and (b) 120 minutes.

XRD patterns indicate the coexistence of SAPO-56 and SAPO-17 at synthesis times of 30 and 120 minutes. SEM images suggest that at 120 minutes, a higher concentration of rod-like shapes (associated with SAPO-17) are present.



	MW (at %)	**Hydrothermal** (at %)
O	65.2	67.3
Al	17.1	16.2
Si	3.1	4.5
P	14.6	12.0

Figure S2. EDX distribution analysis for MW and hydrothermal synthesized samples.

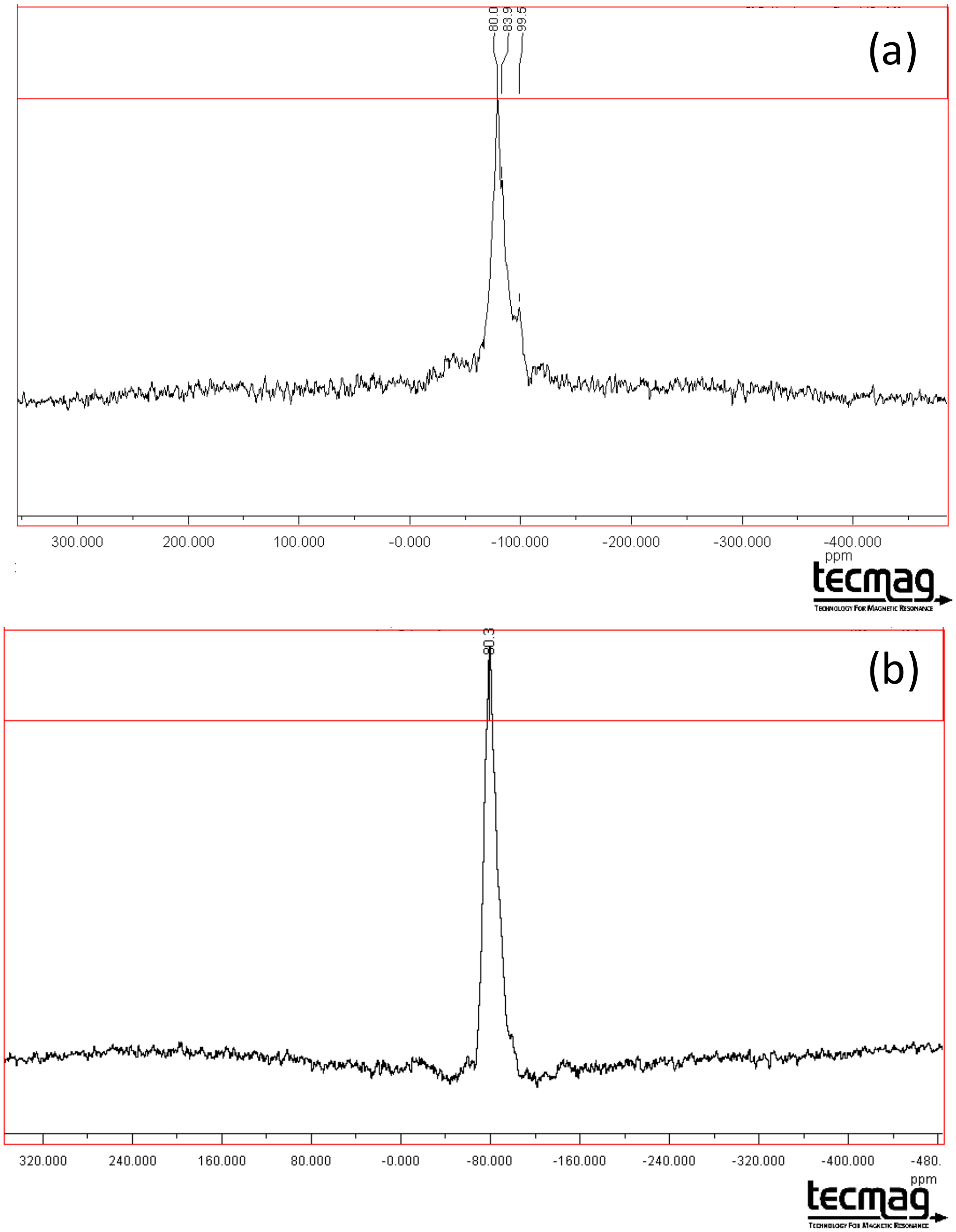


Figure S3. ^{29}Si NMR of (a) MW synthesized and (b) hydrothermally synthesized SAPO-56.

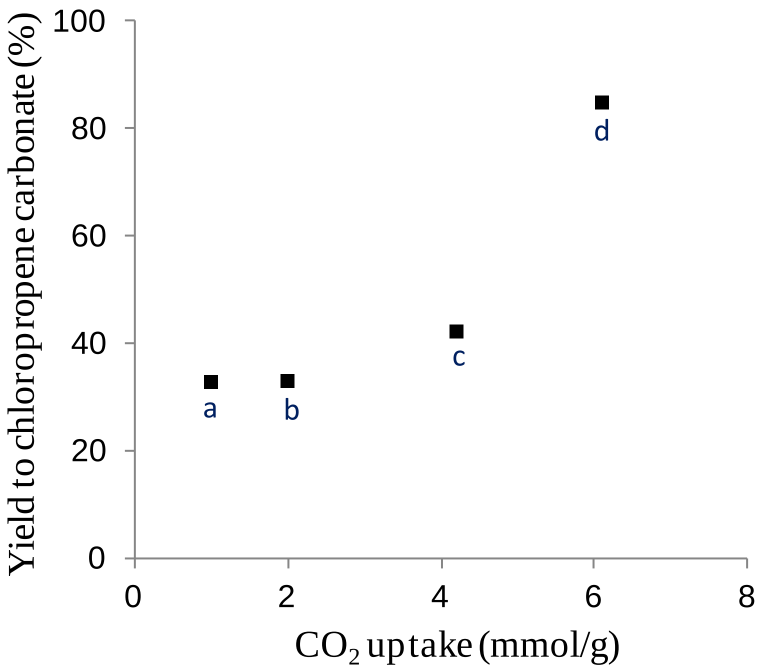
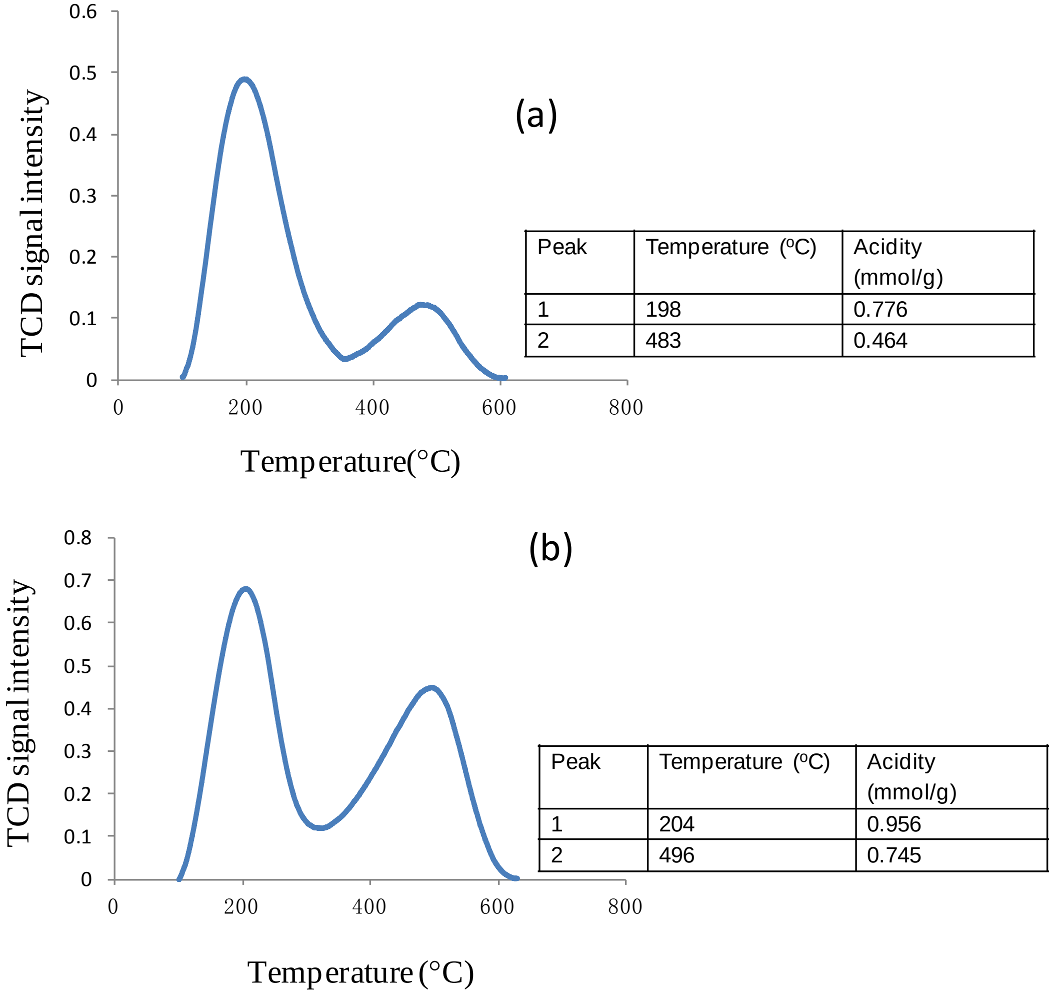


Figure S4. Correlation between Yield to chloropropene carbonate (%) and CO_2 uptake for different catalysts: (a) ZIF-8, (b) Cu-MOF, (c) SAPO-56 (HT), (d) SAPO-56 (MW). Reaction conditions for all catalysts: 100 °C, 4 hr, 18 mmol of epichlorohydrin and 100 mg of catalyst. CO_2 uptakes taken at 400 Torr.

Figure S2 shows that the yield to chlororopropene carbonate correlates with CO_2 uptake. In general the higher the CO_2 uptake the higher the yield to the cyclic carbonate. ZIF-8 and Cu-MOF are metal organic frameworks that were also active for this particular reaction. For the catalytic activity of these two metal organic frameworks refer to: (a) C. Miralda, M. Zhu, E.E. Macias, P. Ratnasamy, M.A. Carreon, *ACS-Catalysis* **2012**, 2, 180 and (b) E.E. Macias, P. Ratnasamy, M.A. Carreon, *Catalysis Today* **2012**, 198, 215-218.



Peak	Temperature (ºC)	Acidity (mmol/g)
1	198	0.776
2	483	0.464

Peak	Temperature (ºC)	Acidity (mmol/g)
1	204	0.956
2	496	0.745

Figure S5. NH_3-TPD of (a) MW synthesized and (b) hydrothermally synthesized SAPO-56.