

Supplementary Information For:

One-step synthesis of honeycomb-like AlPO_4 -11 macrostructures based on epitaxial growth and phase transformation mechanisms

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Synthesis

AlPO₄-11 honeycomb structures were prepared in a eutectic mixture. In a typical synthesis, 4.12 g of diisopropylamine hydrochloride (DIPAC) and 10 g of ethylene glycol (EG) were added to a beaker with stirring at 80 °C for 30 min in an oil bath to form the eutectic mixture. Next, 0.78 g of 1-methylimidazole (1-MIm) and 0.82 g of aluminum isopropoxide (Al[OCH(CH₃)₂]₃) were added with vigorous stirring for 30 min. Finally, 1.39 g of phosphoric acid (85 wt %) was added to the above gel. The reaction gel with the molar composition of 1.0Al[OCH(CH₃)₂]₃/3.0 H₃PO₄/2.31-MIm/7.5DIPAC/40EG was stirred for additional 30 min at 80 °C. Then, the final mixture was transformed into a Teflon-lined stainless autoclave and heated at 160 °C for the required time under static conditions. The solid product was filtered, washed with deionized water, and dried overnight at 100 °C. The as-synthesized samples were calcined in an air at 570 °C for 10 h to remove the templates.

Characterization

Powder X-ray diffraction (XRD) analysis of the as-synthesized samples was performed on a PANalytical X'Pert PRO diffractometer fitted with Cu K α radiation ($\lambda=1.5418$ Å) operating at 40 mA and 40 kV. Scanning electron microscopy (SEM) was carried out on a JSM-7800F field-emission scanning electron microscope or Phenom scanning electron microscope (FEI Electron Optics). Transmission electron microscopy (TEM) images were obtained on a JEM-2100 electron microscope operating at 200 kV. The argon sorption isotherms were measured on a Micromeritics ASAP 2420 analyzer at -186 °C. Prior to the measurements, all of the samples were degassed at 350 °C in a vacuum for 10 hours. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The micropore surface area and micropore

volume were calculated from the adsorption branch based on the t-plot method. The micropore size distribution was calculated from a Satio-Foley (SF) model using the adsorption branch of the isotherm. NMR experiments were performed on a Bruker ADVANCE III 500 spectrometer with a BBO MAS probe operating at a magnetic field strength of 11.7 T. Thermogravimetric (TG) analysis was performed on a NETZSCH STA 449 F3 instrument using dynamic dry air at a flow rate of 50 ml min⁻¹. Elemental analysis was performed on a Thermo Scientific FLASH 2000 Organic Elemental Analyzer. The ²⁷Al MAS NMR spectrum was recorded at 130.3 MHz with a 10 KHz spinning rate. The chemical shift was referenced to a 1% Al(NO₃)₃ aqueous solution. The ³¹P MAS NMR experiment was conducted at 202.5 MHz with a 10 KHz spinning rate. The chemical shift was referenced to 85% H₃PO₄. The ¹³C CP/MAS NMR spectra were recorded at 125.7 MHz with a 6 KHz spinning rate. The chemical shifts were referenced to 2, 2-dimethyl-2-ilapentane-5-sulfonate sodium salt (DSS) for ¹³C.

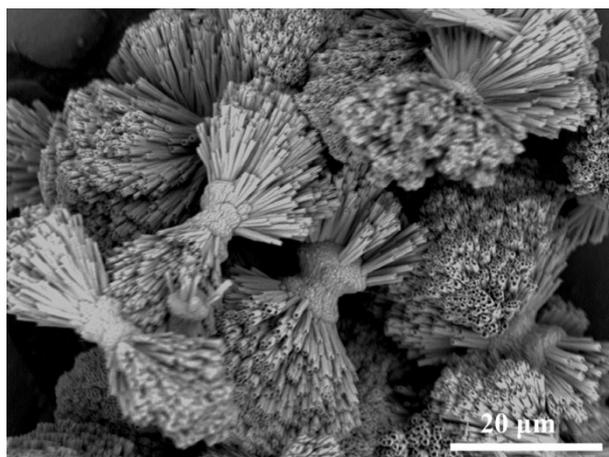


Fig. S1 Low magnification SEM image of the product obtained after reaction at 160 °C for 240 h.

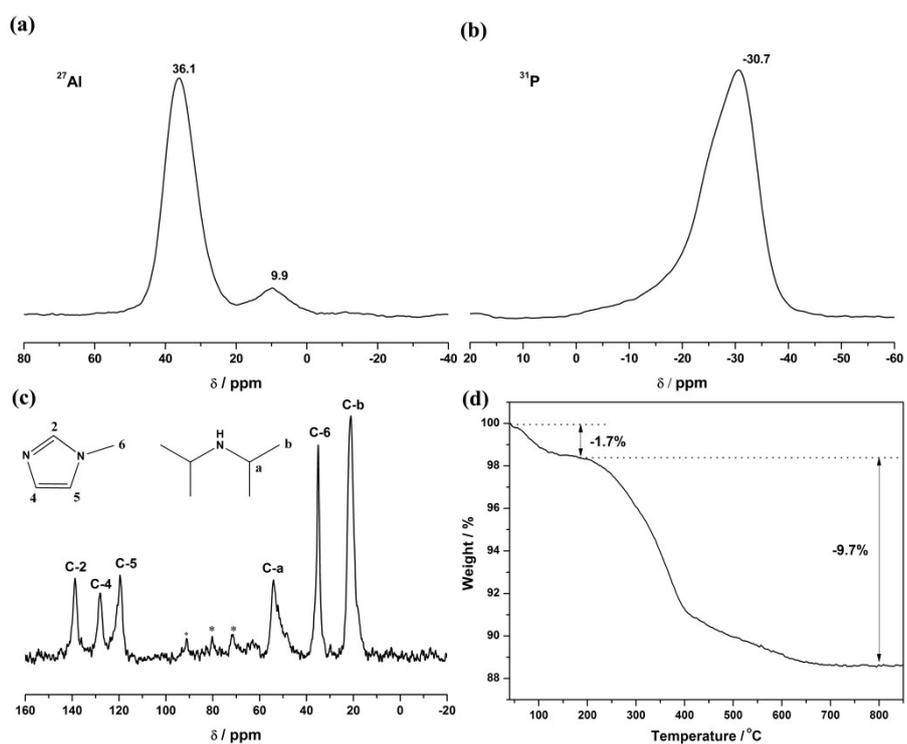


Fig. S2 (a) ^{27}Al MAS, (b) ^{31}P MAS NMR, (c) ^{13}C CP/MAS, * indicates the spinning sidebands and (d) TG analysis of the product obtained after reaction for 240 h.

Table S1. Texture properties of the calcined samples prepared with different reaction times

Reaction time / h	Surface area /(m ² /g)			Pore volume /(cm ³ /g)	
	S _{BET} ^a	S _{micro} ^b	S _{ext} ^c	V _{total}	V _{micro} ^d
3	30	0	30	0.11	0
12	54	8	46	0.15	0.002
24	109	38	71	0.12	0.026
48	154	124	30	0.12	0.046
144	111	80	31	0.09	0.030
240	218	160	58	0.17	0.059

^a BET surface area.

^b t-plot micropore surface area.

^c t-plot external surface area.

^d t-plot micropore volume.

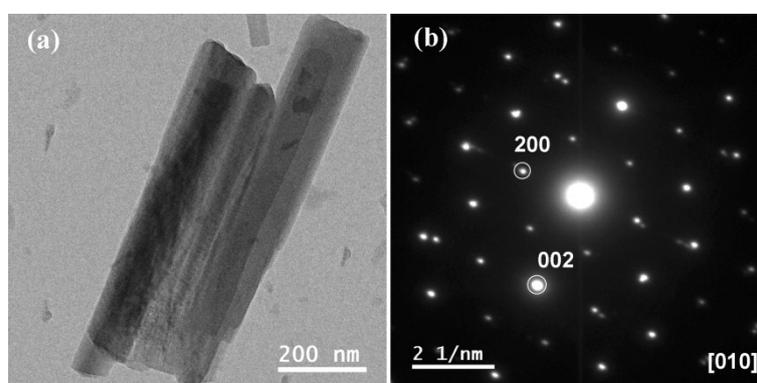


Fig. S3 (a) TEM image of the nanorods attached on the AlPO₄-5 hexagonal prisms obtained after reaction for 24 h and (b) the corresponding SAED pattern.

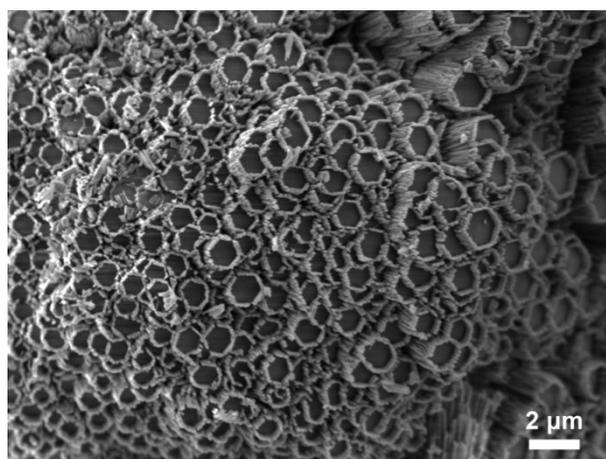


Fig. S4 SEM image of the sample obtained after reaction for 36 h.