Supporting Information

PKU-3: An HCl-Inclusive Aluminoborate for Strecker Reaction Solved by Combining RED and PXRD

Hong Chen,[†,#] Jing Ju,[‡] Qingpeng Meng,[†] Jie Su,[†] Cong Lin,[‡,|] Zhengyang Zhou,[‡,|] Guobao Li,[‡] Weilu Wang,[|] Wenliang Gao,[|] Chunmei Zeng,[|] Chiu Tang,[Γ] Jianhua Lin,*[,‡] Tao Yang,*[,‡,|] and Junliang Sun*[,†,‡]

[†]Berzelii Centre EXSELENT on Porous Materials, Department of Materials and Environmental Chemistry, Stockholm University, 106 91, Stockholm, Sweden
[‡]College of Chemistry and Molecular Engineering, Peking University, 100871, Beijing, China
[|]College of Chemistry and Chemical Engineering, Chongqing University, 400044, Chongqing, China
[Γ]Diamond Light Source Ltd, Didcot, Oxfordshire, OX11 ODE, UK
[#]Faculty of Materials Science and Chemistry, China University of Geosciences, 430074, Wuhan, China

E-mail: junliang.sun@pku.edu.cn; taoyang@cqu.edu.cn; jhlin@pku.edu.cn

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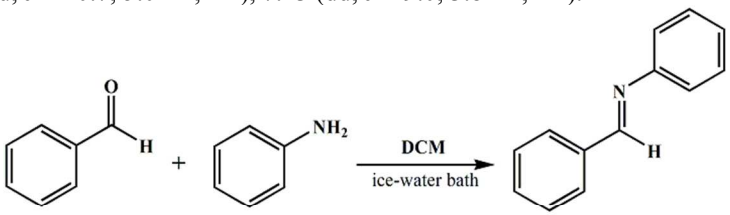
EXPERIMENTS SECTION

Synthesis. All the chemicals are purchased from the company and used as received without further purification. Needle-like PKU-3 crystals with a typical crystal size of 300 nm×300 nm×10 μm were synthesized through the boric acid flux method. In a typical synthesis, 1.2 g $AlCl_3.6H_2O$ (5 mmol), 3.0 g H_3BO_3 (50 mmol) and 0.42 ml concentrated HCl solution (5 mmol) were mixed and ground in a mortar, and then put in a 23 ml autoclave. The mixture was heated at 180 °C for 7 days, and then washed with hot water at 80 °C until the residual boric acid were completely removed. White powder with a yield of 85% based on Al was obtained. Partially replacing the $AlCl_3{\cdot}6H_2O$ with $CrCl_3{\cdot}6H_2O$, the Cr incorporated PKU-3 denoted as Cr-PKU-3 can be achieved with the same structure.

Structure Determination. A carbon film coated copper grid with nano-sized PKU-3 crystals was prepared for collecting rotation electron diffraction (RED) data. A general procedure for preparing the copper grid is that, around 5 mg powder sample was crushed manually in a mortar. The crushed powder was transferred into a test tube with 5 ml absolute ethanol. After ultrasonic treatment for 10 minutes, 2 drops of the suspension was added on a carbon film coated copper grid and dried in air under 1 kW lamp heating for 5 mins. The prepared grid can be used directly for RED data collection. RED data was collected on a JEOL JEM2100 TEM with very low dose electron beam by using the second condenser aperture. A single tilt sample holder with ±70° goniometer tilt was used. The TEM and camera were controlled by the RED program automatically[1] and electron diffraction patterns were recorded by an Gatan ES500W Erlangshen camera. The dataset was collected on a 520×650×500 nm sized crystal with the tilt angle range from -60° till 50° and the exposure time of 0.5 s. The goniometer tilt step is 2°, and the beam tilt step is 0.1° with the beam tilt range of ± 1.1°. In total, 1264 frames were recorded, which were then used to construct the whole reciprocal space for the data reduction by the program RED. High resolution synchrotron PXRD data used for the unit cell and structure refinement was collected at the Beamline I11 at Diamond Light Source U.K.[2] The ab-initio structure solution and refinement based on RED data were done by SHELX 97,[3,4] and the electron wavelength and the atomic scattering factors for electrons were used in the refinement against the RED data.

Adsorption Experiments. Adsorption and desorption isotherms of N_2 was measured using a Micromeritics ASAP2020 device at 77 K. In order to obtain the Cl^--washed PKU-3, the sample was washed with a mixture solution of $NH_3{\cdot}H_2O$ and KOH. For a typical procedure, 1 g as-synthesized PKU-3 was added into 60 ml 26 wt% $NH_3{\cdot}H_2O$ mixed with 0.1 g KOH, the mixture solution was kept stirring at 40 ℃ for 4 h, and then the solid was filtered and dried. Prior to the adsorption measurements, the Cl^--washed PKU-3 was activated under dynamic vacuum conditions at 393 K for 12 hours.

Catalytic Property Test. The synthesis of N-(phenylmethylene)-benzenamine (1): In a typical reaction run, aniline (32 mmol) is added to a mixture of benzaldehyde (30 mmol) and DCM (dichloromethane, 45 ml) in a 100 ml flask. After 30 minutes, anhydrous magnesium sulphate (62 mmol) is added into the flask. Then, the ice-water bath is removed and the reaction mixture is stirred at room temperature for a given time. The resulted mixture is then filtered through a Busher funnel. The filtrate is refluxed with Et_2O in an oil bath at 35 °C. Then, the product is obtained at -5 °C。 ^{1}H NMR spectra were recorded on Bruker AV-500 in the deuterated solvent. (^{1}H chemical shifts are reported in ppm (δ) with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.24 ppm). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.46 (s, 1H), 7.93-7.88 (m, 1H), 7.50-7.46 (m, 1H), 7.40 (dd, J = 10.7, 5.0 Hz, 1H), 7.23 (dd, J = 9.0, 3.8 Hz, 1H).



Scheme S1. Synthesis of N-(phenylmethylene)-benzenamine.

The synthesis of α-(phenylamino)-benzeneacetonitrile (2): PKU-3 (0.2 equiv.) was added into a stirred mixture of the specified solvent (1 mL), TMSCN (0.4 mmol) and 1 (0.2 mmol) at room temperature. The mixture was stirred for 3 hour. Progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was quenched with saturated $NaHCO_3$ queous solution, extracted with DCM for three times, dried with $MgSO_4$ and concentrated under reduced pressure. Yields were determined by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, CDCl3) δ: 7.63-7.59 (m, 2H), 7.50-7.43 (m, 3H), 7.31-7.26 (m, 2H), 6.97-6.86 (m, 1H), 6.79 (dd, J = 8.5, 0.9 Hz, 2H), 5.44 (d, J = 8.4 Hz, 1H), 4.02 (d, J = 8.2 Hz, 1H).

Other Characterizations. The chemical analysis based on inductively coupled plasma (ICP) analysis was carried on an ESCALAB2000 analyzer. Energy dispersive X-ray spectra were recorded on a LaB_6 TEM from 20 different crystals. Combine with this two techniques, it gives the Al:B:Cl ratio of 9.0:16.7:3.3, close to the one in the structure model. PXRD data for characterization the crystallinity and phase were collected at room temperature with a Bruker D8 diffractometer with Bragg-Brentano geometry with a curved germanium primary monochromator (Cu Kα1, λ=1.54056 Å), the tube voltage and current were 50 kV and 40 mA,

respectively. The IR spectrum was recorded with a Nicolet Magna-IR-750 spectrometer. Thermogravimetric (TG) analysis was conducted using a Perkin-Elmer TGA7 under nitrogen atmosphere in a platinum crucible between 20 and 800 °C at a heating rate of 10 °C min^{-1}. The ^{27}Al and ^{11}B NMR spectra were recorded on a Bruker AV300 using conventional Bruker probes.

Referneces

(1) Wan, W.; Sun, J.; Su, J.; Hovmöller, S.; Zou, X.; Hovmo, S. *J. Appl. Crystallogr.* **2013**, *46*, 1863–1873.

(2) Thompson, S. P.; Parker, J. E.; Potter, J.; Hill, T. P.; Birt, A.; Cobb, T. M.; Yuan, F.; Tang, C. C. *Rev. Sci. Instrum.* **2009**, *80*, 075107.

(3) Sheldrick, G. M. Program for Solution of Crystal Structures **1997**.

(4) Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112–122.

Table S1. Crystallographic data of PKU-3 and refinement details of RED data collection, structure solution and refinement.

Crystal system	Trigonal
Space group	*P*-3*c*1
Cell parameters [Å]	a = 14.67 (1), b =14.67(1), c =12.40(8), α = 90.24, β = 90.62, γ = 119.78
Cell volume [Å^3]	2312.87(3)
Crystal shape/colour	needle, colourless
Crystal size [μm]	0.3 × 0.3 ×10
Diffractometer/radiation	JEOL 2100 TEM LaB_6 200KV, λ=0.0251Å
Tilt range[°]	-60° / 50 °
h,k,l	$-15 \le h \le 16$, $-16 \le k \le 16$, $-14 \le l \le 13$
Measured reflections	5972
Completeness[%]	96.8%
Resolution[Å]	0.84
Structure solution method	Direct method
Independent reflections	1171
Independent reflections (>4σ)	138
R_{int}	0.4822
Constraints/restraints	0/0
R_1 [$F_o \ge 4\sigma(F_o)$]	0.1395
R_1 (all data)	0.3744
Weighting scheme	$w^{-1}=\sigma^2 F_o^2+(0.2000P)^2$ With $P=(F_o^2+2F_c^2)/3$
Max./min. residual	0.288/-0.353

Table S2. Crystallographic data, experimental and refinement details of the synchrotron PXRD for PKU-3

Identification code	PKU-3
Temperature	150(3) K
Wavelength	0.82613(1) Å
X-ray source	Beamline I11, Diamond
Crystal system	Trigonal
Space group	*P*-3*c*1
Unit cell dimensions	*a* = 14.58438 (1) Å *c* = 12.22262 (2) Å
Volume	2251.494(6) $Å^3$
2Theta range for refinement	3.0 - 68 º
Number of parameters	101
Refinement method	Rietveld refinement
*R*p/*R*wp/*R*exp (%)	4.71/6.23/3.26
R_1 (%)	3.16
GOF	1.91

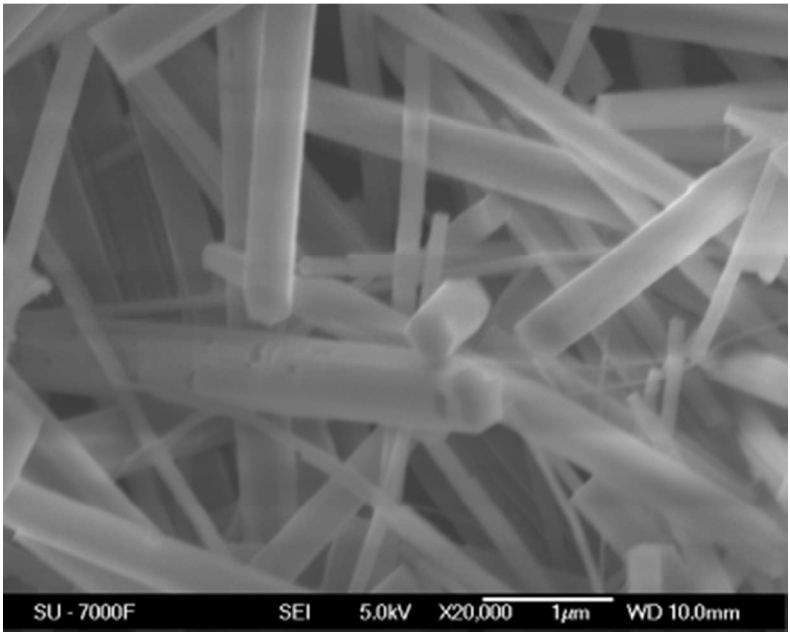


Figure S1. The SEM image of as-synthesized PKU-3.

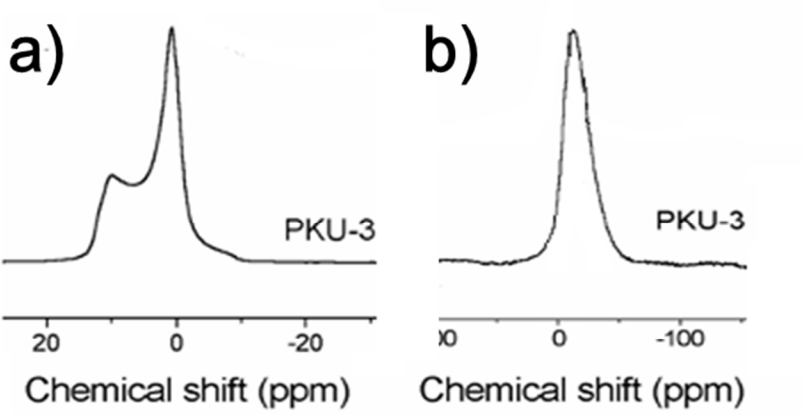


Figure S2. The ^{11}B and ^{27}Al NMR of PKU-3.

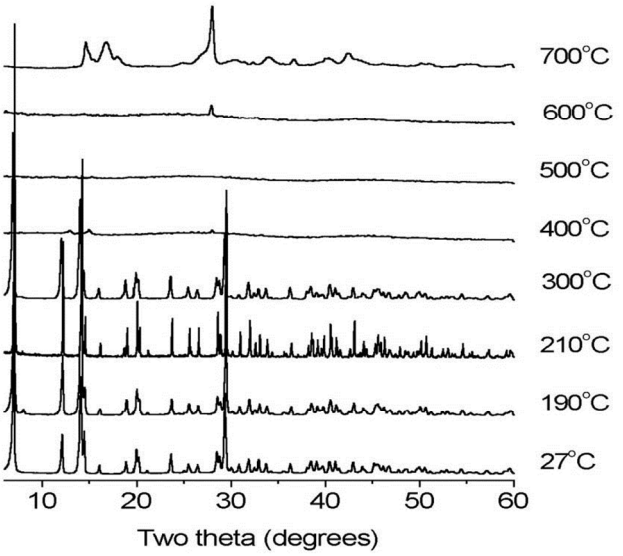


Figure S3. In-situ PXRD of PKU-3.

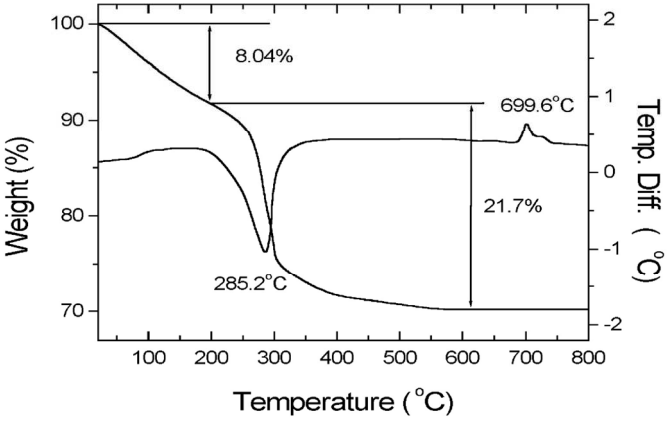


Figure S4. TG-DSC of PKU-3.

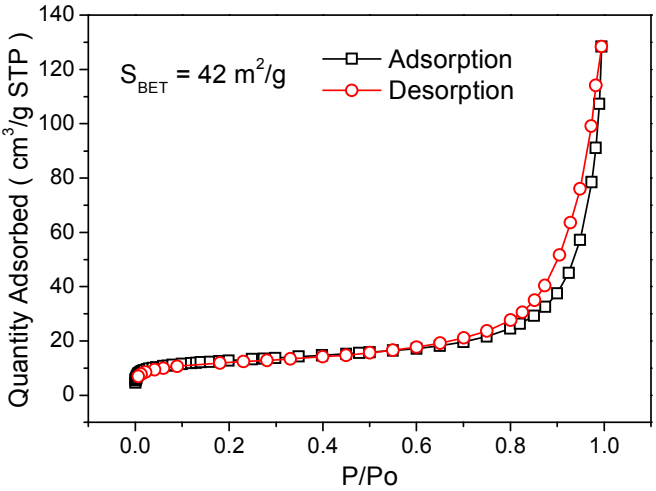


Figure S5. N_2 adsorption and desorption isotherm of PKU-3 after washed by pure water.

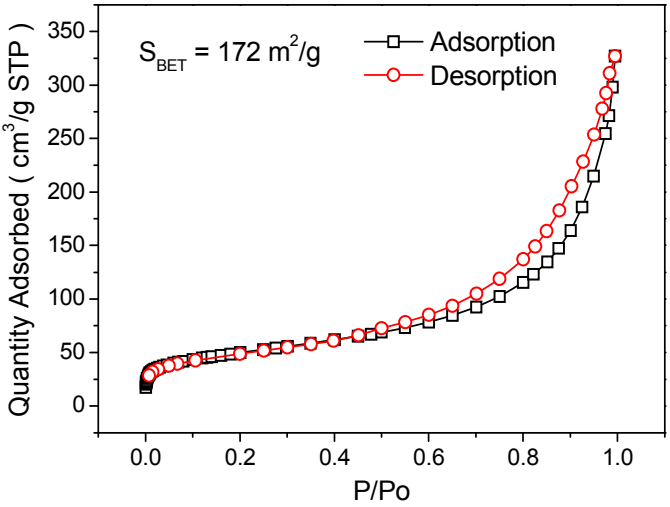


Figure S6. N_2 adsorption and desorption isotherm of PKU-3 after washed by $NH_3 \cdot H_2O$ and KOH mixture solution.

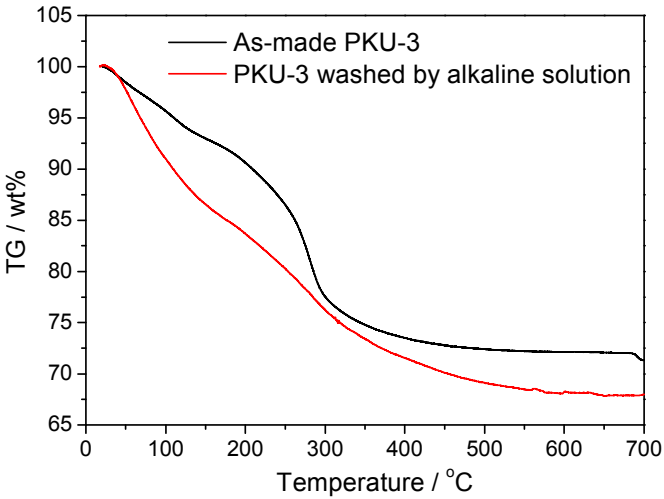


Figure S7. TG curves of as synthesized PKU-3 and after washed by $NH_3 \cdot H_2O$ and KOH mixture solution.

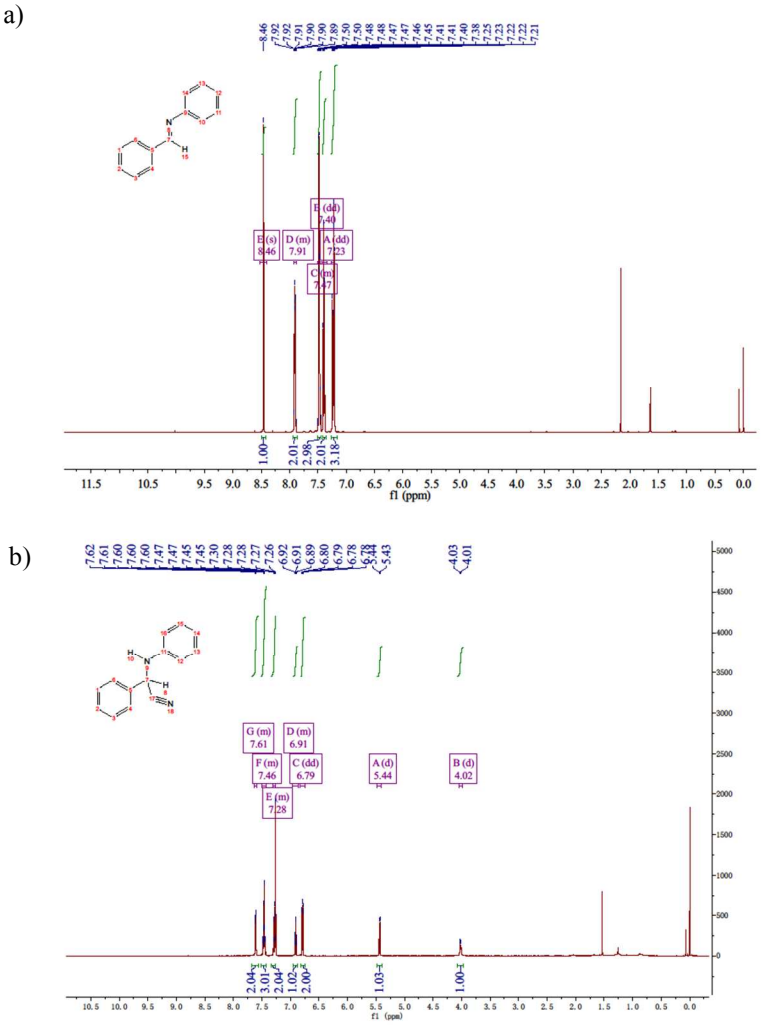


Figure S8. ^{1}H NMR spectra of reactant and product, a) Reactant (1); b) Product (2).

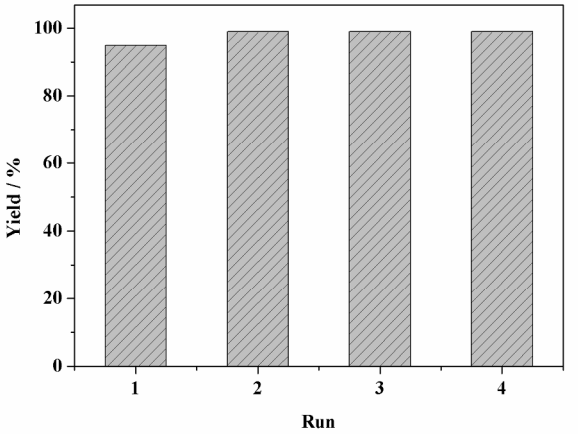


Figure S9. Recyclability test of PKU-3 in the Strecker reaction. After each circle, Cr-PKU-3 was recovered by filtration, washed and dried, and then re-used for a new batch with fresh reagents.