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,[∥] 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

[∥]Diamond Light Source Ltd., Didcot, Oxfordshire OX11 ODE, U.K.

[⊥]Faculty of Materials Science and Chemistry, China University of Geosciences, 430074 Wuhan, China

S *Supporting Information*

ABSTRACT: A novel microporous aluminoborate, denoted as PKU-3, was prepared by the boric acid flux method. The structure of PKU-3 was determined by combining the rotation electron diffraction and synchrotron powder X-ray diffraction data with well resolved ordered Cl^- ions in the channel. Composition and crystal structure analysis showed that there are both proton and chlorine ions in the channels. Part of these protons and chlorine ions can be washed away by basic solutions to activate the open pores. The washed PKU-3 can be used as an efficient catalyst in the Strecker reaction with yields higher than 90%.

Inorganic microporous materials such as zeolites, phosphates, borates, and germanates have attracted significant attentions due to their diverse porous structure and wide applications in adsorption, catalysis, and separation.[1−9] These materials are normally synthesized with structure directing agents (SDAs), and their formation heavily relies on the chemical interaction, such as hydrogen bonds and ionic interaction between the SDAs and the framework. SDAs such as polyamines have strong interactions with the framework, and the obtained materials frequently show bigger crystal sizes but their open-frameworks can hardly be retained after the calcination. A typical class of this material is germanates. On the contrary, the frameworks synthesized with the weakly interacted SDAs are much more stable after calcination, such as silicate zeolites. Aluminoborates is a type of materials where both strongly (the alkali/alkaline earth metal ions, organic amines, etc.) and weakly interacted SDAs (boric acid, water etc.) can be employed in the synthesis.[10−19] When weakly interacted species such as H_3BO_3, H_2O are involved in the channels, the obtained aluminoborates are stable after calcination and can be used as catalysts in different reactions.[13,16,20]

Unfortunately, aluminoborates synthesized with weakly interacted guest species normally crystallized in small sizes, and most of their structures were difficult to be elucidated by single crystal X-ray diffraction (SC-XRD).[16−19,21−24] Powder X-ray

diffraction as an alternative method to SC-XRD could be used to solve the structures with tiny crystal sizes as demonstrated in our former studies in PKU-1,[13] PKU-5,[23] PKU-6,[19] PKU-8,[24] etc. However, there are still a lot of reported aluminoborates without knowing atomic structures.[17,18,21,22] One typical example is PKU-3 in this work, which was synthesized more than 10 years ago without a structure model. The sample shows preferred orientation with a needle-like morphology, and the severe peak overlapping due to the trigonal symmetry ($P\bar{3}c1$) and relatively large unit cell dimensions. Fortunately, the recently developed rotation electron diffraction (RED) method can be used to collect the 3D electron diffraction data for nanosized crystals,[25] and it requires significantly lower electron dose compared to the HRTEM imaging. However, one remaining problem in RED data is the residue dynamical effects, which sometimes hinder the structure determination.[7,26−29] Therefore, combining the 3D data feature of RED to partition the kinematic PXRD data is a superior way, which would expect to reduce the difficulties created by dynamical effects in RED and overlapping reflections in PXRD. Here, we report the structure of aluminoborate PKU-3, with the formula $H_{24.3}Al_9B_{18}O_{51}\cdot Cl_{3.3}\cdot 6.8H_2O$, which contains the light atoms down to B, solved by combining RED and PXRD. The framework and even the ordered Cl^- species in the channel can be well resolved. Additionally, PKU-3 shows a rarely seen acidic framework with inclusive HCl. Due to the similar Lewis acidity to PKU-1 and PKU-2, PKU-3 can be used as a solid acid catalyst in the Strecker reaction for the synthesis of α-aminonitriles.

PKU-3 was synthesized by the boric acid flux method with a mixture of $AlCl_3\cdot 6H_2O$, H_3BO_3, and concentrated HCl solution reacted in a 23 mL autoclave at 180 °C for 7 days. Needle-like PKU-3 crystals with a typical size of 0.3 × 0.3 × 10 μm (Figure S1) were harvested after washing with hot water at 80 °C. In addition, the partially Cr-doped PKU-3 named as Cr-PKU-3 has also been synthesized by using $CrCl_3\cdot 6H_2O$ to replace part of $AlCl_3\cdot 6H_2O$.

The attempt of ab initio structure determination by high resolution synchrotron PXRD data from the DIAMOND light source was performed in EXPO 2009.[30] Only three Al and a few oxygen atoms could be directly located. The reasons for the failure of obtaining light atomic positions include the complexity of the diffraction pattern (such as the relatively large unit cell dimensions (with $a = 14.58438$ (1) Å and $c = 12.22262$ (2) Å) and the severe peak overlapping due to the trigonal symmetry (86% within 0.2 fwhm below 1.0 Å resolution)),[31] flexible coordination environments for boron atoms, and the disordered heavy chlorine anions in the channel. The RED method[25,32] was then employed to collect 3D electron diffraction data sets on the crushed nanosized PKU-3 crystal. An overview of the RED data is shown in Figure 1a, and a trigonal unit cell with the possible
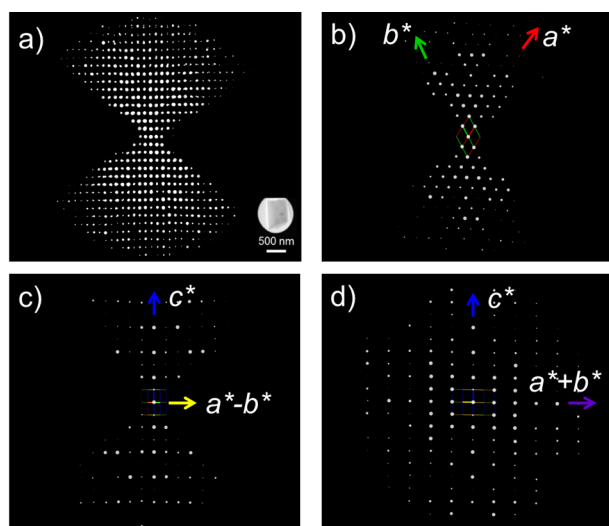

Figure 1. Reconstructed 3D RED data. (a) Overview of the data and the nanocrystal used to collect the RED data; due to the electron beam damage, the reflections at high resolution following the clockwise direction become weaker and weaker. (b−d) Selected planes in the reciprocal lattice corresponding to hk0, h-hl, and hhl planes, respectively. The reflection conditions can be obtained as h-hl, l = 2n, 00l, l = 2n. Due to the dynamical effects, some weak reflections violate the reflection conditions.

space group of $P\bar{3}c1$ could index the whole data set as shown in Figure 1b−d. With the RED data, ab initio structure determination by direct methods was successfully applied in both SIR2011[33] and Shelxs 97.[34] Although some oxygen atoms were assigned as Al and the ordered Cl⁻ ion was assigned as B, the whole framework structure can be obtained by correcting the element types and refined using Shelxl as shown in Table S1. The wrong assignment of element types might be due to the residue dynamical effects in RED data. Since the intensity summations for overlapping reflections are very accurate in the synchrotron data, we used RED data to repartition overlapping PXRD reflections, and in such a combination, we took both advantages of the nonoverlapping feature in RED and more accurate intensities in PXRD. As expected, most framework atoms and an ordered Cl⁻ ion in the pores can be obtained directly with correct element assignments (Al/Cl or B/O) by Shelxs 97. To the best of knowledge, this is the first time that the atoms in the channel of the open framework can be well resolved from RED data. Besides, we can also conclude that even with a high R_{int} for RED data ($R_{int} = 0.48$ in this case), its intensities can be used to partially solve the overlapping problems in the PXRD data, which

results in a SC-XRD-like data for the structure solution by Shelxs. After the structure model of PKU-3 was derived, all the non-hydrogen atoms in the structure model were further refined against the PXRD data by the Rietveld refinement in TOPAS 4.0 with $R_p = 0.0471$, $R_{wp} = 0.0623$, and $R_{exp} = 0.0326$ (Figure 2).[35] The obtained crystallographic data of PKU-3 and refinement details are listed in Table S2.
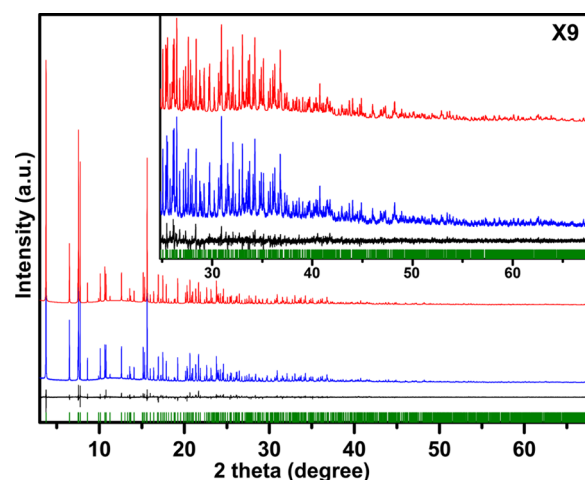

Figure 2. Rietveld refinement of powder X-ray diffraction for as-synthesized PKU-3 ($\lambda = 0.82613(1)$ Å). The curves from the top to bottom in red, blue, and black are calculated, observed, and difference curves, respectively.

PKU-3 is built with the structure building unit (SBU) of $[Al_3B_6O_{24}]$ as shown in Figure 3a. This SBU includes three edge
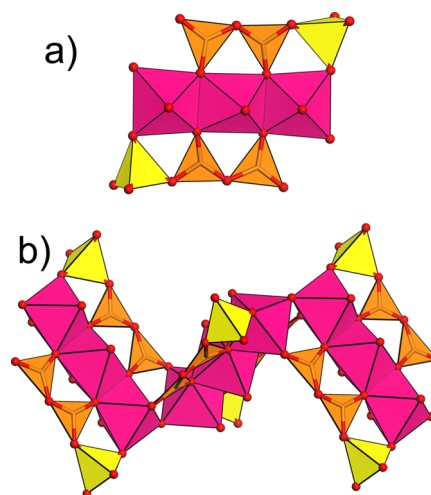

Figure 3. Building unit of PKU-3. (a) $[Al_3B_6O_{24}]$ SBU; (b) Zig-zag chain along the c-axis: AlO_6 (pink octahedron), BO_3 (orange triangle), and BO_4 (yellow tetrahedron).

shared AlO_6 octahedra with two BO_3 triangles and one BO_4 tetrahedron on each side. The ordered BO_3 and BO_4 units were confirmed by solid state ^{11}B magic angle spinning (MAS) NMR (peaks at 0.9 and 10.0 ppm, respectively, in Figure S2a), obviously different from the disordered BO_3 contained borates such as NDTB-1.[36] The ^{27}Al MAS NMR showed that all Al atoms are octahedrally coordinated with a peak at $\delta = -10.9$ ppm seen in Figure S2b, consistent with the structure model obtained from diffraction experiments.[16] Two different 3-rings exist in the

$[Al_3B_6O_{24}]$ SBU: one is the AlO_6–BO_3–BO_3 ring, which was commonly seen in PKU-1[13] and PKU-2;[16] the other is AlO_6–BO_4–BO_3 ring, which was also found in PKU-8. These $[Al_3B_6O_{24}]$ SBUs are connected to each other to form a composite columnar building unit along the c-axis by sharing the oxygen atoms in AlO_6 octahedra and BO_3 triangles (Figure 3b). These columns are further connected to each other through BO_4 tetrahedra (Figure 3b), forming a three-dimensional (3D) structure as shown in Figure 4a. Two one-dimensional channels
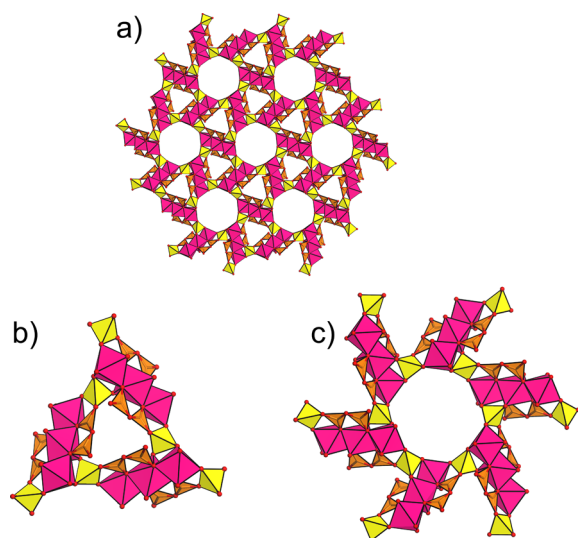

**Figure 4.** Three-dimensional framework of PKU-3: (a) view along c-axis; (b) 9-ring and (c) 12-ring.

with different sizes are present in PKU-3 along the c-axis: the small 9-ring channel with three SBUs in Figure 4b has a free diameter of 0.47×1.96 Å; the large 12-ring channel with six SBUs has a free diameter of 6.41×5.57 Å (Figure 4c), taking into account of the van der Waals radius of oxygen 1.35 Å.

Based on the refinement, EDS, and TGA-MS results, the channels of PKU-3 are occupied by Cl^- ions and water. In the small 9-ring channel, one ordered Cl^- ion was located directly from the structure solution, while in the 12-ring channel, only disordered Cl^- and water molecules were found, and disordered oxygen atoms with large ADPs were used to mimic their scattering power in the refinement. The EDS results showed Al/Cl molar ratio of about 2.7(6), and this additional 1.3 Cl^- ion should be located in the 12-ring channel in a disordered form. Note that the large standard deviation of Al/Cl molar ratio may be due to occupancy fluctuation of the disordered Cl^- in the channel and the error of the EDS technique. Thus, the formula could be written as $H_{24.3}Al_9B_{18}O_{51} \cdot Cl_{3.3} \cdot 6.8H_2O$, where the amount of water was determined from TGA and the amount of hydrogen atoms were calculated based on the charge balance of the whole structure. Ion-exchange experiments show that the H^+ and Cl^- in PKU-3 can be partially exchanged by K^+ and Br^- without destroying the framework structure, indicating a special HCl inclusive feature for PKU-3. Compared to other synthesized microporous material structures with monocharged species,[3,36,37] neutral structure direct agents[38] or salts[39–41] included in the structural channel, the H^+ and Cl^- inclusive feature in PKU-3 is unique. The only known example with both protons and acid anions in the channel, similar to PKU-3, is the natural mineral akaganeite, which is constructed from FeO_6 octahedra with H^+ and Cl^- in its 8-ring channels.[42]

In order to explore the application of this framework material, $NH_3 \cdot H_2O$ and KOH mixed solution was used to wash the as-synthesized PKU-3 in order to evacuate the channel, and part of HCl can be removed with the surface area increasing from 42 to 172 m^2/g compared to the as-synthesized PKU-3 (Figures S5–S7). The EDS result for the washed PKU-3 showed Al/Cl molar ratio of about 6.1 (6), indicating that all Cl^- in the 12-ring channel and part of Cl^- in the 9-ring channel can be removed. The in situ PXRD in Figure S3 shows that the framework of PKU-3 is stable up to 300 °C in air, consistent with the observation in the TG-DSC curve (Figure S4). Compared with PKU-1 and PKU-2 where the framework is mainly built with edge sharing AlO_6, the lower thermal stability of PKU-3 may be due to the corner sharing between the $[Al_3B_6O_{24}]$ SBUs or the easy volatility of HCl in channels.

Similar to the Lewis acidity in PKU-1 and PKU-2,[16,43] the framework of PKU-3 with the BO_3 (or B_2O_5, BO_2OH) groups potentially provides both Lewis and Brønsted acid sites. This specific feature makes PKU-3 an attractive candidate as a solid acid catalyst in the Strecker reaction for the synthesis of α-aminonitriles (Scheme 1). As shown in Table 1 (entry 1–3), it

Scheme 1. Cyanosilylation of N-(Phenylmethylene)-benzenamine Catalyzed by PKU-3[a]
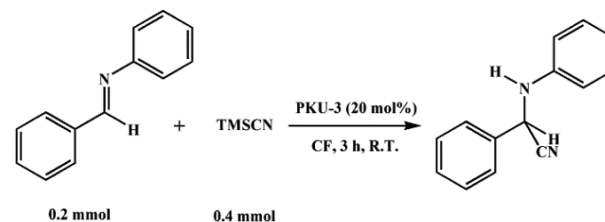
[a]TMSCN: Trimethylsilyl cyanide.

Table 1. Yields of Cyanosilylation by PKU-3 and Cr-PKU-3[a]

entry	catalyst	solvent	yield[b]
1	PKU-3	DCM	79%
2		CF	87%
3		acetonitrile	74%
4	Cr-PKU-3	DCM	99%
5		CF	93%
6		acetonitrile	92%

[a]Reaction conditions: N-(phenylmethylene)-benzenamine (0.2 mmol), TMSCN (0.4 mmol), solvent (1 mL), catalyst (20% equiv), 3 h, RT. [b]Yield was determined by ^{1}H NMR.

shows the highest yield (87%) of α-aminonitriles in chloroform (CF) within 3 h, which indicates that nonpolar solvent is beneficial to this reaction. Note that the blank experiment in CF (without adding any solid catalyst) shows no yield at all. It is consistent with the results in literature,[44,45] where the uncatalyzed reactions show only trace conversion. It has been proved that the Strecker reaction can be effectively catalyzed by heterogeneous catalysts either containing solid acid sites or transition metal centers,[46] and therefore, chromium doped PKU-3 (denoted as Cr-PKU-3) can be considered as a bifunctional catalyst with more active centers. Indeed, Cr-PKU-3 has a superior activity (Table 1, entry 4–6) in all used solvents; the yield of α-aminonitriles reaches 99% in DCM within 3 h. Moreover, we did not observe any appreciable loss in the catalytic

activity of Cr-PKU-3 catalyst after four runs (Figure S9), which approves the recyclability of PKU-3 in the Strecker reactions.

In summary, a novel aluminoborate framework denoted as PKU-3 was successfully synthesized. The structure was determined by the combination of RED and synchrotron PXRD, and this combination was proved to be as powerful as single-crystal X-ray diffraction. The ordered Cl^- can be resolved from RED-aided PXRD data. The inclusive H^+ and Cl^- feature of PKU-3 was also confirmed. Benefiting from the Lewis and Brønsted acid feature, PKU-3 shows great catalytic activity in the Strecker reaction from cyanosilylation to imine.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and crystal structure information files. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03685.

■ AUTHOR INFORMATION

Corresponding Authors
*junliang.sun@pku.edu.cn
*jhlin@pku.edu.cn
*taoyang@cqu.edu.cn

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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