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Microporous Catalysts

Microporous Aluminoborates with Large Channels: Structural and Catalytic Properties**

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Zeolites and related porous materials are widely used as acid catalysts for a large number of reactions.[1,2] Furthermore, the molecular dimensions of the pores can provide size selectivity for certain chemical transformations of molecules that are smaller than the pores or of comparable size to the pore dimensions, which is a unique phenomenon happening in porous materials.[2] The microporosity of catalysts, however, may also restrict the diffusion rates of the reactants and products, thereby limiting the activity.[3] It is well-known that the diffusivity is proportional to the pore diameter. Large pores increase the diffusion coefficients, thereby increasing the potential of the material as an effective catalyst. It is therefore highly desirable to prepare materials with large pores. PKU-1 ($HAl_3B_6O_{12}(OH)_4{\cdot}n\,H_2O$), a porous aluminoborate with channels formed by 18 octahedrally coordinated atoms,[4] contains B and Al centers that can serve as Lewis acid sites.[5] Herein we present the synthesis and structure determination of a new aluminoborate, PKU-2 ($Al_2B_5O_9(OH)_3{\cdot}n\,H_2O$), with larger channels formed by 24 octahedrally coordinated atoms. Both PKU-1 and PKU-2 possess large pores and Lewis acid centers, thus making them potential candidates for heterogeneous catalysts. The topologies of PKU-1 and PKU-2 are the same, but the former consists of 18-ring channels, and the latter contains extra-large pores of 24-ring channels, which makes the two materials intriguing representative examples to study the reactivity and selectivity versus the pore size by investigating the catalytic performance.

PKU-2 was synthesized by direct reaction of $AlCl_3{\cdot}6\,H_2O$ with H_3BO_3 heated to reflux at 240 °C in a closed system. Only very tiny needle-shaped crystallites were obtained (Figure S1 in the Supporting Information). Attempts to grow larger single crystals by varying the B/Al ratio and extending the reaction time were unsuccessful. Poor crystallization is also indicated by the broad peaks observed in the powder X-ray diffraction (XRD) pattern (Figure 1 a), which can be easily indexed to be trigonal using a hexagonal unit cell, $a = 30.489(2)$ Å and $c = 7.013(1)$ Å. The systematic absences and intensity distribution in the electron diffraction (ED) patterns fit the space groups $R3$ or $R\bar{3}$ (Figure S2 in the Supporting Information). Owing to the low quality of the XRD data and the relatively large unit cell of PKU-2, the detailed structure could not be solved directly. However, the high-resolution transmission electron microscopy (HRTEM) image taken along the [001] direction of PKU-2 (Figure 1 b) and the similarity of the cell parameters to PKU-1 ($a = 22.038$ and $c = 7.026$ Å), allowed us to propose a reasonable structure model.

In our previous work, we described a structural rule that applies to aluminoborate systems with octahedral-based frameworks:[4,6] two types of unique connections between AlO_6 octahedra (*cis* and *trans*) were considered to be the building units for this type of porous frameworks (Figure S3 in the Supporting Information). Herein, the similar *c* parameters of PKU-1 and PKU-2 indicate that the AlO_6 octahedra connected in a *cis* geometry form the same threefold helical chains along the *c* axis, and the approximately 8.5 Å larger *a* parameter in PKU-2 suggests that the hexagonal channels are larger. Therefore, by inserting an additional *trans*-AlO_6 unit into each of the six 18-ring edges in PKU-1, we proposed that the AlO_6 backbone of PKU-2 contains 24-ring channels (Figure 1 c). This assumption is supported by the HRTEM image along the *c* axis, which agrees well with the image produced by simulation by using such a structure model (inserted in Figure 1 b).

The BO_3 borates are crucial for the charge balance that stabilizes the Al octahedral framework.[4,6] The characterization of PKU-2 by ^{27}Al and ^{11}B magic-angle-spinning NMR (MAS NMR) and IR spectroscopy (Figures S4 and S5 in the Supporting Information) indicates that the Al and B atoms are coordinated in octahedral and trigonal-planar geometry,

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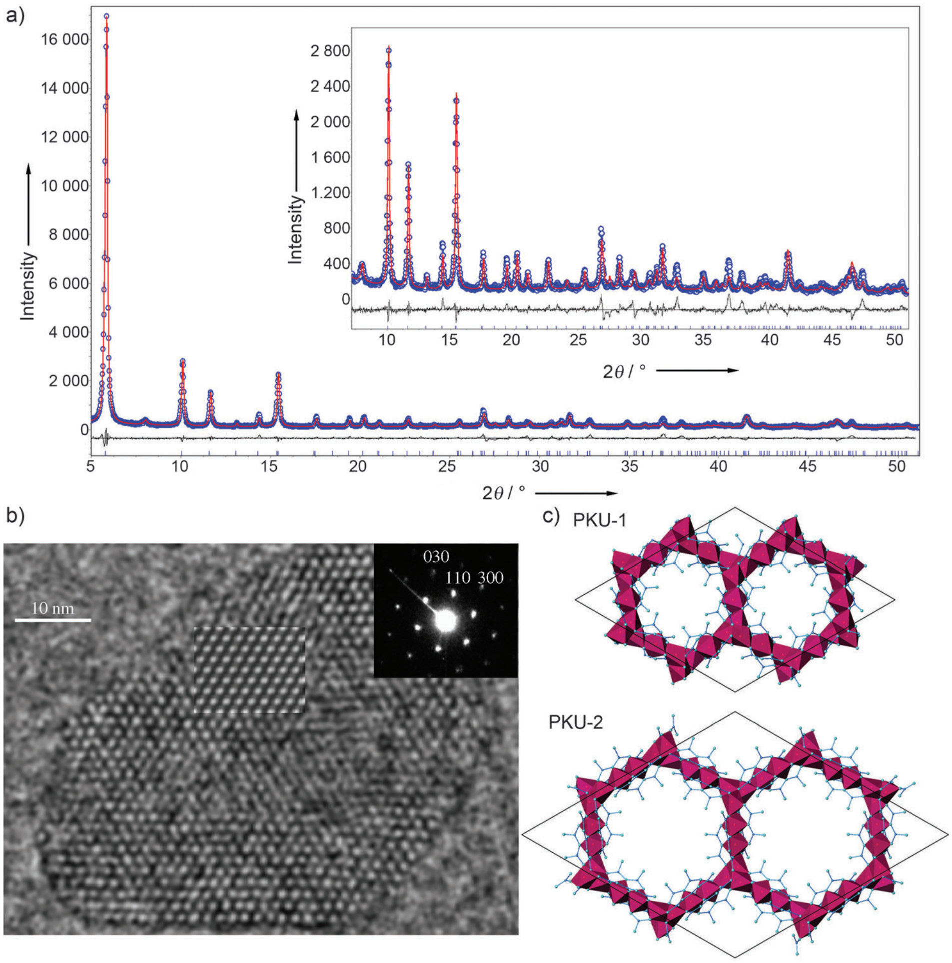
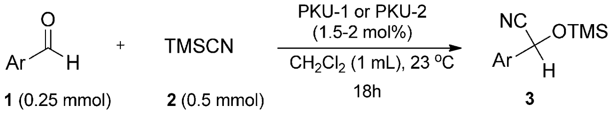


Figure 1. a) Rietveld refinement on powder X-ray diffraction of PKU-2; b) HRTEM image along the [001] direction of PKU-2 showing the 24-ring channels (white features). Insets are the corresponding ED pattern (right) and a simulated image based on the structure model (left); c) projected structure views of both PKU-1 and PKU-2 along the *c* axis, showing the 18- and 24-ring channels, respectively.

respectively. The geometry of the octahedral framework in PKU-2 seems able to accommodate dimeric and trimeric borate groups B_2O_5 and B_3O_7. Simulated annealing was performed using the TOPAS software[7] with the borate groups treated as rigid fragments. A good fit of the Rietveld refinement (Figure 1 a) can be achieved using the above-mentioned structure model (Figure 1 c); the refined parameters are given in the Supporting Information. As expected, all oxygen atoms in the Al octahedral frameworks in PKU-2 are coordinated to boron through two different 3-ring units, either $2\,AlO_6 + BO_3$ or $AlO_6 + 2\,BO_3$, which is the same as in PKU-1 (Figure S6 in the Supporting Information). The slight difference is that in PKU-1 only the borate group B_2O_5 is present, while both B_2O_5 and B_3O_7 can be found in PKU-2. This difference is consistent with the expansion of the channel size. Although the structure is deduced by a chain of soft evidence, the final refined structure agrees well with the structural and chemical principles, that is, with reasonable Al–O, Al–Al, Al–B, and O–O distances (Table S3 in the Supporting Information).

On the basis of the crystallographic study, the framework composition of PKU-2 is determined to be $Al_2(B_2O_5)(B_3O_7)$. Considering the charge balance, the formula should be $Al_2B_5O_9(OH)_3$. Thermogravimetric analysis shows a two-step weight loss (see the inset of Figure S7 in the Supporting Information). The first approximately 17.4 wt % loss below 200 °C corresponds to the loss of guest water molecules in the channels. The second weight loss (ca. 8.6 wt %) at approximately 500 °C corresponds to the dehydration of the borate groups (calculated 8.9 wt %). The in situ high-temperature XRD measurements show that the framework of PKU-2 is retained up to 400 °C (Figure S7 in the Supporting Information). The nitrogen adsorption isotherm of PKU-2 exhibits a typical microporous behavior with a large BET surface area ($900\,m^2\,g^{-1}$, Figure S8 in the Supporting Information).

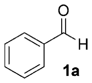
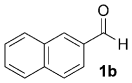
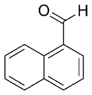
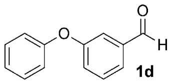
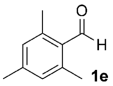
The B and Al atoms of PKU-1 and PKU-2 can act as Lewis acid sites[5] and thus coordinate the oxygen atom of aldehydes, which increases their reactivity towards nucleophilic attack. The Lewis acid catalyzed cyanosilylation reaction of aldehydes was chosen to study the catalytic activity of the two frameworks (Scheme 1).[8,9] In this transformation, highly versatile cyanohydrin trimethylsilyl ethers are produced, which can be readily converted into important compounds such as α-hydroxycarboxylic acids or β-amino alcohols.[10]



Scheme 1. Cyanosilylation of aldehydes catalyzed by PKU-1 or PKU-2.

Both PKU-1 and PKU-2 were first washed with water at 40 °C for four hours to remove the remaining boric acid species from the pores. After filtration, the samples were dried under vacuum at 110 °C for another four hours. After cooling to ambient temperature under a nitrogen atmosphere, the frameworks were tested as heterogeneous catalysts. The results are shown in Table 1. Benzaldehyde gave high yields of the corresponding cyanohydrin trimethylsilyl ether after 18 h at ambient temperature in the presence of either PKU-1 or PKU-2 (1.5–2 mol %; Table 1, entry 1). More sterically

Table 1: Cyanosilylation of a variety of aldehydes (**1 a**–**e**) catalyzed by PKU-1 and PKU-2.[a]

Entry	Aldehyde (**1**)	Yield of **3** [%][b] PKU-1	Yield of **3** [%][b] PKU-2
1	 **1a**	93	100
2	 **1b**	23/75[c]	34/86[c]
3	 **1c**	10	47
4	 **1d**	27	98
5	 **1e**	9	26

[a] PKU-1 or PKU-2 (20 mg, 0.020 mmol, 1.5–2 mol%) was dried under vacuum for 4 h at 110 °C. After cooling the sample to 23 °C under a nitrogen atmosphere, a solution of trimethylsilyl cyanide (140 μL, 1 mmol) and aldehyde (0.5 mmol) in degassed dichloromethane (1 mL) was added. The reaction mixtures were stirred at 23 °C. [b] Unless otherwise noted, the yield was determined by ^{1}H NMR spectroscopy of the crude mixture after 18 h. [c] Yield after three days.

demanding substrates, such as **1b**–**e** (Table 1, entry 2–5), gave lower conversions after 18 h in the presence of either PKU-1 or PKU-2. Only after three days, good conversions were obtained with both catalysts (Table 1, entry 2). With PKU-2 as the catalyst higher conversions were obtained in all cases, which may be explained by the larger pore dimensions of this framework. However, such differences in activity could also be caused by the different particle size of the two materials: the average particle size of PKU-1 is 2 × 2 × 20 μm, which is much larger than that of PKU-2 (50 × 50 × 200 nm). To minimize the difference in particle size between the two materials we grinded a sample of PKU-1 to the size of (150 ± 50) nm, which is comparable to the size of PKU-2. We then performed the cyanosilylation reaction of substrate **1d** in two parallel experiments under identical reaction conditions using both frameworks (now with similar average particle size). The reaction conditions were identical to those of Table 1, and very similar results were obtained (i.e. 13% using PKU-1, 97% using PKU-2). This experiment indicates that the activity of PKU-1 is not significantly affected by the particle size, and that PKU-2 shows a significantly higher catalytic activity than PKU-1.

To confirm that the reaction was catalyzed by the frameworks and not by homogeneous Al or B species leached into the solution, further control experiments were performed. The reaction of benzaldehyde (**1a**) with TMSCN (**2**) catalyzed by PKU-1 and PKU-2 was started as described in Table 1, and after four hours the catalysts were removed by filtration. Conversions of 21% and 38% had been reached with PKU-1 and PKU-2, respectively, after these four hours. The reaction mixtures were stirred for additional three days after removal of the heterogeneous catalysts. Analysis of the crude mixtures by ^{1}H NMR spectroscopy revealed a 25% conversion for PKU-1 and 48% for PKU-2. Thus, after three days in the absence of the solid frameworks the conversions remained almost the same as those obtained after four hours in the presence of the catalysts. This result demonstrates that the reaction is only catalyzed by the heterogeneous catalysts and not by homogeneous species present in the reaction media. Moreover, both heterogeneous catalysts PKU-1 and PKU-2 could be recycled and reused up to five times (Table 2) without any decrease of the catalytic activity, thus suggesting high stabilities of the catalysts.

Table 2: Recycling and reuse of PKU-1 and PKU-2 in the cyanosilylation of benzaldehyde (**1 a**).[a]

Catalyst	Yield of **3** [%][b] run 1	run 2	run 3	run 4	run 5
PKU-1	86	72	80	88	84
PKU-2	97	100	100	100	100

[a] See the Experimental Section. [b] The yield was determined by ^{1}H NMR spectroscopy of the crude mixture after 20 h.

In summary, we have synthesized the 3D porous octahedral framework PKU-2 ($Al_2B_5O_9(OH)_3{\cdot}n\,H_2O$), which contains extra-large 24-ring channels. The structure model of PKU-2 was deduced from its topological similarity to PKU-1 and further refined by powder X-ray diffraction. The model was also confirmed by ^{27}Al and ^{11}B MAS NMR and IR spectroscopy as well as HRTEM. The catalytic activity of PKU-1 and PKU-2 as Lewis acids was investigated in the cyanosilylation reaction of aldehydes under mild reaction conditions. Both frameworks are highly active for the cyanosilylation of small substrates, whereas only PKU-2 with larger channels formed by 24 octahedrally coordinated atoms catalyzes the reaction for larger substrates.

Experimental Section

Synthesis of PKU-2: Typically, $AlCl_3{\cdot}6H_2O$ (5 mmol) and H_3BO_3 (100 mmol) were sealed into a 50 mL Teflon autoclave and the mixture was heated at 240 °C for 15 days. After cooling to room temperature, the solids (containing the PKU-2 and residue H_3BO_3) were washed extensively with hot water (50 °C) until the residual boric acid was completely removed (yield 90% with respect to Al). Since PKU-1 and PKU-2 can be synthesized under similar conditions, the dependence of the products on reaction temperatures, time, and the B/Al ratio in the systems were extensively studied. PKU-1 formed easily at relatively low temperatures and in the first few days. Once the reaction temperature was elevated to at least 240 °C with longer reaction time (more than 10 days), the chance to form PKU-2 either as an admixture with PKU-1 or a pure phase increased. Chemical analysis carried out by using the ICP method on an ESCALAB2000 analyzer showed that the B/Al ratio (ca. 2.3) was consistent with the proposed formula $Al_2B_5O_9(OH)_3{\cdot}n\,H_2O$.

Characterizations: Powder-XRD data were collected at room temperature with a Bruker D8 diffractometer with Bragg–Brentano geometry with a curved germanium primary monochromator (Cu $K_{\alpha 1}$ $\lambda = 1.5406$ Å). The tube voltage and current were 50 kV and 40 mA, respectively. Scan step size and time: 0.02 (2θ) and 30 s. For TEM investigations, the PKU-2 powder was crushed in a mortar and suspended in ethanol (99.9 vol.%) by ultrasonication. The suspension was dropped onto a holey carbon film. HRTEM and selected area electron diffraction (SAED) were performed with a 300 kV electron microscope (JEM-3010) at low magnification and under very low electron dose to minimize radiation damage. Owing to their needle-like shapes, very few crystals of PKU-2 could be oriented in such a way that the needle direction (the *c* axis) was parallel to the electron beam so that the 24-ring channels could be observed. HRTEM images and SAED patterns were recorded with slow-scan CCD cameras.

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