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Introduction

Strecker reactions have attracted considerable attention in recent years because of their extensive implications in the preparation of α -amino acids, biologically active molecules, and nitrogen or sulfur-containing heterocycles.^{1,2} Among them, homogeneous systems are commonly employed due to their excellent enantioselectivity as well as high yields, however the major deficiency lies in the difficulty in catalyst separation and reutilization, workup scalability and discarding waste.³ In order to avoid the above problems, various solid catalysts have been investigated in the past decades, including metal–organic frameworks (MOFs),^{4–6} supported complexes,^{7–9} solid bases,¹⁰ molecular sieves,^{11,12} acid-modified catalysts,^{13,14} polymers,^{15,16} nano-sized materials,¹⁷ and solid oxides.^{18,19} For example, metal–organic frameworks (MOFs) provide a promising catalysis-friendly process in Strecker synthesis, benefitting from their large surface areas,

Continuous solid solutions constructed from two isostructural octahedron-based molecular sieves: preparation, acidity regulation and catalytic application in Strecker reactions[†]

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Strecker reactions have an important application in the preparation of α -amino acids and biologically active molecules in homogeneous acid- or base-catalyzed systems. As novel solid acid catalysts, Al_xGa_{1-x}-PKU-1 (x = 0-1) solid solutions constructed by two octahedron-based molecular sieves were prepared by using a molten boric acid method and exhibited a continuously-adjustable acidity in heterogeneously-catalyzed Strecker reactions under mild conditions. Al_xGa_{1-x}-PKU-1 accommodated a large number of Brønsted acid sites in the framework, and the acidic density and strength were enhanced with the successive incorporation of Al atoms, thus the catalytic activity became superior in the formation of α -aminonitriles. Three-fold coordinated boron atoms, despite the electron-deficient configuration, seemed unable to behave as Lewis acid centers probably due to steric hindrance against the adsorption of large organic substrates. This work illustrates, for the first time, possible application in Strecker reactions using zeolite-like solid solutions, and will potentially provide an effective method and a beneficial reference to control surface acidity for porous materials.

readily accessible cavities and extensive porosity, however, the main drawbacks are their rather low thermal and chemical stability.^{4–6} The supported homogeneous catalysts have also been developed as solid acids for Strecker reactions, however because of the strong tendency of H_2O coordination to acidic sites, the catalytic centers gradually became inactive probably due to the formation of Lewis acid–base adducts.^{7–9} In general, the common feature of these employed catalysts is to possess a certain amount of acidic and/or basic sites, and usually, some post-treatment methods, such as surface sulfonation, ion exchange, dealuminization, metal doping, *etc.* are needed to enhance or regulate their surface acidity/basicity.

In addition to the above-mentioned post-treatment modifications, preparing solid solutions is also regarded as an effective method to control surface acidity/basicity for porous materials. Making solid solutions is very common in the synthesis of bulktype oxides, however it is rare when synthesizing molecular sieves or zeolite-like ones. Herein, we intend to report continuous solid solutions composed of two octahedron-based molecular sieves (Ga-PKU-1 and Al-PKU-1), featuring ultra-large channels with an 18-membered ring window.^{20,21} In particular, the surface acidity was proven to be continuously tunable with successive metal substitutions. As a matter of fact, during the last decades, several octahedron-based aluminoborate molecular sieves (such as PKU-2 and PKU-3) have also been synthesized using the molten boric acid method.^{22–26} However, thus far, only PKU-1 has been



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extensively studied in catalysis,^{27–32} benefitting from its easy preparation, easy metal substitution and high density of acidic sites or redox centers. Because of the features in the structure and functional diversity, PKU-1 is a good candidate to accommodate a large number of Brønsted or Lewis acid sites to promote Strecker reactions. From this perspective, compared to other heterogeneous catalysts, as-designed continuous solid solutions are a good alternative to allow an environmentally friendly process under mild conditions. As expected, the obtained catalytic results showed that the reconstructed hybrid catalysts can efficiently control the amounts and strength of the acid sites, and also proved to be efficient catalysts in the Strecker reaction with excellent yields of α -aminonitriles and an added advantage of catalyst recyclability.

Single crystal X-ray diffraction revealed that the framework of Ga-PKU-1 is exclusively constructed by edge-sharing GaO₆ octahedra, and an 18-membered-ring channel is formed along the [001] direction.²¹ In order to neutralize the negative charges of the Ga-O framework, three types of borate hydroxyl groups attach to the GaO₆-framework in the form of BO(OH)₂, BO₂(OH) and $B_2O_4(OH)$ fragments. Further investigations indicated that Al can replace Ga in the whole concentration range to form complete solid solutions (denoted as Al_xGa_{1-x} -PKU-1, $0 \le x \le 1$). Due to the obvious difference in atomic configuration between Ga and Al, these as-prepared solid solutions tend to exhibit a tunable acidity with the increase of x. As shown in Fig. 1, the framework of PKU-1 seems to provide two kinds of acidic centers, one is the Brønsted acid site coming from borate hydroxyl group B-OH, and the other one is the Lewis acid site originating from the Al³⁺/Ga³⁺ ion or BO3 group. Structurally speaking, AlxGa1-x-PKU-1 can be considered as a solid acid, thus it has potential to heterogeneouslycatalyze the synthesis of α -aminonitriles.

In this study, Al_xGa_{1-x} -PKU-1 ($0 \le x \le 1$) molecular sieves were synthesized using a molten boric acid method and were further evaluated in the Strecker reactions. The nucleophilic addition of imines by cyanide ions was gradually strengthened with the increase of Al concentration. A catalytic survey also evidenced that Al_xGa_{1-x} -PKU-1 only offers a single type of acidic site, *i.e.* Brønsted acid sites (B–OH). Three-fold coordinated boron atoms, despite their electron deficiency, seemed not to behave as Lewis acid centers



Fig. 1 Octahedron-based framework of PKU-1 with 18-membered ring windows along the [001] direction; Grass green octahedron, AlO_6 or GaO_6 ; orange plane triangle, BO_3 ; cyan sphere, O atom; grey sphere H atom.

according to the fact that a poor catalytic activity was observed after losing the B–OH groups (by heating Al_xGa_{1-x} -PKU-1). This is presumably due to the steric hindrance against the approach of large organic substrates. Nevertheless, when Al_xGa_{1-x} -PKU-1 was calcined at a higher temperature to transform into another so-called mullitetype structural phase, a large number of Lewis acid or Lewis base sites were created due to the unsaturated AlO_5 or GaO_5 groups in the framework. At last, the reaction mechanism for Strecker reactions was also proposed to illustrate the reaction paths catalyzed over Al_xGa_{1-x} -PKU-1 solid solutions.

Experimental section

Preparation

In a typical run for the preparation of $Al_{0.5}Ga_{0.5}$ -PKU-1, 5 mmol of β -Ga₂O₃ and 10 mmol of $Al(NO_3)_3$ ·9H₂O were dissolved in 2 mL of concentrated HNO₃ and heated in a sealed autoclave at 180 °C for 5 h. After cooling, the autoclave was opened to evaporate the liquid slowly and 0.3 mmol of H₃BO₃ was added. The autoclave was sealed again and heated at 220 °C for another 5 days. After the reaction, the obtained solid was washed extensively with warm water until the residual boric acid was completely removed. The final product after drying at 80 °C was a white powder with a high yield (>90%) according to metal sources. Other Al_xGa_{1-x} -PKU-1 samples with different Al/Ga compositions were prepared in a similar procedure. For simplicity, all these as-synthesized samples were denoted as Ga-PKU-1, $Al_{0.2}Ga_{0.8}$ -PKU-1, $Al_{0.5}Ga_{0.5}$ -PKU-1, $Al_{0.8}Ga_{0.2}$ -PKU-1 and Al-PKU-1.

Characterization

Powder X-ray diffraction (PXRD) measurements were performed using a PANalytical Empyrean powder diffractometer (Cu K α radiation, λ = 1.5406 Å) with an operating voltage of 40 kV and a current of 40 mA. Le Bail fitting was performed using the TOPAS software package.³³ The surface morphology was determined by field emission scanning electron microscopy (JEOL, JSM-7800F), which was equipped with an energy dispersive spectrometer (EDS) analyzer. The powder samples were prepared by casting the suspension of material onto a double-sided conductive adhesive tape. The thermal stability of Al_xGa_{1-x}-PKU-1 was studied using a Mettler-Toledo TGA/DSC1 instrument in high purity nitrogen from room temperature to 900 °C with a ramping rate of 10 °C min⁻¹. Temperatureprogrammed desorption of ammonia (NH3-TPD) was performed using a Quantachrome ChemBET Pulsar instrument equipped with a TCD detector to test their acidic properties. Typically, Al_xGa_{1-x} -PKU-1 samples were treated with helium for 1 h before the adsorption experiment of NH₃. Then, the sample was saturated in 5% NH₃/He-mixed gas (80 mL min⁻¹) at 100 °C for 60 min. Helium was used as a carrier gas at a constant flow rate in the temperature range from 100 °C to 527 °C at a ramping rate of 10 °C min⁻¹ after removing the weaklyphysisorbed NH₃ by flushing helium for 30 min. The desorbed NH_3 was absorbed by a standard solution of H_2SO_4 (0.01 M), which was then titrated with NaOH (0.001 M) for ascertaining

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the amount of acidic sites in the presence of the indicator of phenolphthalein. Fourier transformation infrared (FT-IR) spectra were collected using a NICOLET iN10 MX (in the range 1000–3800 cm⁻¹) to measure the framework vibration of the as-prepared materials. ¹H NMR and ¹³C NMR data were recorded using a Bruker Avance (500 MHz) or Agilent VNMRS 400 MHz at 25 °C with dimethyl sulfoxide- d_6 (DMSO) as the solvent. High-resolution mass spectrometry was performed on a Bruker solarix 7.0 T and by the ESI-FTICR-MS method.

Experimental procedure for the synthesis of *a*-aminonitriles

Organic solvents were purified by the distillation method using CaH_2 or Na as a desiccant. Other reactants were used as received. Analytical thin layer chromatography (TLC) was performed to monitor the reaction process using Merck 0.2 mm silica gel 60 F-254 Al-plates (200–300 mesh). The following abbreviations are used to record NMR spectroscopic data: s = singlet, d = doublet, t = triplet, m = multiplet, and dt = doublet of triplets. ¹H NMR spectra of the products were used to determine the yield of the obtained compounds.

Typical procedure for the syntheses of *N*-tosyl aldimine precursors. Scheme 1 shows the reaction equation for the synthesis of *N*-tosyl aldimine precursors. 4-Methyl-benzenesulfonamide (12 mmol) was added into a 50 mL flask containing the mixed solution of toluene (25 mL) and benzaldehyde (10 mmol). While refluxing the solution at 110 °C for 60 min, 2 mmol of BF₃OEt₂ was slowly added into the reaction mixture. After quenching with NaOH solution (1 M), the reaction solution was extracted with ethyl acetate three times, washed with brine several times, and dried over anhydrous Na₂SO₄. Then, the mixture was concentrated to obtain the primary product. In some cases, this primary product was purified using flash column chromatography to afford a pure substrate, 4-methyl-*N*-phenylmethylenebenzenesulfonamide (1a).

If using 2,4,6-trimethyl-benzaldehyde, 3,4-dimethyl-benzaldehyde, 3,4-dimethyl-benzaldehyde or 4-(1-methylethyl)-benzaldehyde as a starting reagent, the corresponding precursor noted as **1b**, **1c**, **1d** or **1e** was obtained. The spectrum data of these 5 precursors agreed well with the reported ref. 27, indicating their successful synthesis, and the ¹H and ¹³C NMR data of these 5 precursors and the HRMS of the two compounds are listed in the ESI.[†]

Typical procedure for the cyanation of N-tosyl aldimines catalyzed by Al_xGa_{1-x}-PKU-1 catalysts. Scheme 2 shows the reaction equation for the cyanation of N-tosyl aldimines. At room temperature (R.T.), a mixture of a specified solvent (1 mL), cyanotrimethylsilane (TMSCN) (0.4 mmol), 1a (1b, 1c, 1d or 1e, 0.2 mmol) and $Al_{x}Ga_{1-x}$ -PKU-1 (0.2 equiv., x = 0, 0.20, 0.20, 0.200.50, 0.80, 1.00) was stirred for 3 h under a N₂ atmosphere. After the reaction was completed, the mixture was first quenched with saturated NaHCO3 aq., then extracted with dichloromethane three times, dried with MgSO4 and further concentrated under a reduced atmosphere. The obtained products were labeled as 2a (2b, 2c, 2d or 2e), and their yields were determined by ¹H NMR of aldimines. The spectrum data of these 5 products agreed well with the reported ref. 27, indicating their successful synthesis, and the ¹H and ¹³C NMR data of all products and the HRMS of the two compounds are also listed in the ESI.[†]

Results and discussion

Catalyst syntheses and characterization

Powder XRD spectra of these as-synthesized Al_xGa_{1-x}-PKU-1 materials are shown in Fig. 2a, and all curves exhibited similar diffraction patterns with that of the parent sample (Ga-PKU-1). All these patterns can be indexed using the trigonal cell lattice in the space group R3, indicating that metal Al and Ga can mutually substitute to form continuous solid solutions in the whole concentration range. The unit cell parameters including a, c and V of the other four samples were also calculated from Le Bail refinements and exhibited a linear contraction along with the increase of Al content (see Fig. 2b), which coincides with the fact that the ionic radius of Al^{3+} (0.535 Å, coordination number (CN) = 6) is smaller than that of Ga^{3+} (0.620 Å, CN = 6). As a representative, the XRD pattern of Al_{0.2}Ga_{0.8}-PKU-1 was used to calculate its cell parameters with TOPAS software and showed a good convergence (see Fig. 2c). For an exact observation, when the strongest diffraction peaks of Al_rGa_{1-r}-PKU-1 at $2\theta = \sim 8^{\circ}$ (Miller indices (110)) were enlarged, the gradual shift to lower 2θ angle can be clearly observed with the increase of Al content (the inset of Fig. 2c). The above results provide convincing evidence of the successful formation of continuous solid solutions in the entire concentration range.



Scheme 1 Synthesis of 1a precursor using 4-methylbenzenesulfonamide and benzaldehyde as reactants.



Scheme 2 Strecker reaction between N-tosyl aldimines and TMSCN catalyzed over Al_xGa_{1-x}-PKU-1.



Fig. 2 (a) PXRD patterns of Al_xGa_{1-x} -PKU-1; (b) calculated cell parameters *a*, *c*, and *V* by Le Bail refinements; (c) Le Bail fitting for $Al_{0.2}Ga_{0.8}$ -PKU-1. The blue circles \bigcirc and red solid line represent the observed and calculated patterns respectively; the difference curve (in black) is also shown below the diffraction curves. The inset gives the strongest peak (110), which shows a gradual shift to lower angles with the increase of *x*.

SEM was employed to observe the morphology of the asprepared Al_xGa_{1-x} -PKU-1 samples. As shown in Fig. 3, the type and amount of metal element have an important influence on the sample morphology, and Ga seems able to increase the crystallization and gives a more orderly arrangement. As for Ga-rich samples, a slender fascicular-arranged crystalline morphology was thermodynamically preferred, while the densely-packed rod-liked crystals tend to be formed for aluminum-rich PKU-1 samples. The relative metal content of as-synthesized Al_xGa_{1-x} -PKU-1 was determined using energy dispersion spectro-



Fig. 3 SEM images of as-prepared Al_xGa_{1-x} -PKU-1 samples. (a) x = 0; (b) x = 0.2; (c) x = 0.5; (d) x = 0.8; (e) x = 1; (f) EDS analysis of the $Al_{0.8}Ga_{0.2}$ -PKU-1 sample. The values in red are the atomic ratios of Ga/Al determined by EDS analysis.



Fig. 4 NH₃-TPD measurements of the as-prepared Al_xGa_{1-x} -PKU-1 solid solutions.

scopy (EDS), as indicated in Fig. 3, where the measured molar ratios of n(Ga)/n(Al) are in good agreement with the proportion used in the starting materials.

NH₃-TPD was employed to monitor the acidity evolution for all Al_xGa_{1-x}-PKU-1 catalysts. Generally speaking, the temperature of NH₃ desorption is related to the acidic strength, while the integration area below the curve corresponds to the amount of acid sites.³⁴ As shown in Fig. 4, these different Al_xGa_{1-x}-PKU-1 solid solutions display very different acidic properties. In the whole temperature range, all Al_xGa_{1-x}-PKU-1 samples only give a single desorption peak, and the NH₃-desorption peaks shift towards high temperatures with the increase of *x*. That is to say, the acidic strength becomes stronger with the successive incorporation of Al atoms. Fig. 4 also gives the amount of acidic sites, and these quantitative data indicate that the introduction of Al³⁺ results in a linear increase in the number of total acid sites. PKU-1 with a higher aluminum content probably has a better performance in catalytic Strecker reactions.

The thermal behaviors of Al- and Ga-PKU-1 catalysts were measured by thermogravimetric analysis (TGA), and both TGA curves show a two-step weight loss in the whole temperature range from 27 to 900 °C. As shown in Fig. 5, the first step centered at \sim 110 °C or \sim 120 °C should come from the release of weakly-absorbed water molecules and the dehydration of



Fig. 5 Thermal behaviors of Al-PKU-1 and Ga-PKU-1.

 $\rm H_3BO_3$ dispersed inside the channels; the second one centered at ~372 °C or 364 °C, however, is probably attributed to the dehydroxylation of borate hydroxyl groups located in the framework. Despite the similarity in the decomposition temperature, Al-PKU-1 has a larger total weight-loss percentage than Ga-PKU-1 (nearly twice), which denotes that the former has more hydroxyl groups in the framework than the latter and therefore can provide more sufficient Brønsted acid sites.

Catalytic performance

Hereinafter, Al_xGa_{1-x} -PKU-1 solid solutions with different Al contents were used as the solid acids to survey the catalytic nucleophilic addition of the cyanide anion to imines in the Strecker reactions. TMSCN was chosen as the cyanide source because it is an effective, safe and easily-handled cyanation reagent compared to HCN and alkali cyanides. Under the given reaction conditions, imine 1a was first used as the model reactant to react with TMSCN, and the obtained catalytic results are given in entries 1-5 of Table 1. With the increase of Al concentration, the yields of 2a grew quickly, and the completely Al-substituted PKU-1 (Al-PKU-1) is nearly 4 times more active than Ga-PKU-1. Such a catalytic activity tendency is obviously related with the acidic properties of Al_xGa_{1-x} -PKU-1. As indicated by NH₃-TPD, there was a successive increase in both acidic strength and acidic amount along with the incorporation of Al atoms; it seems that Al atoms can bring more active sites to activate the nucleophilic addition of imines. In addition, the scope of the Strecker reaction was extended to different imine substrates, and the other 4 aromatic imines were employed to react with TMSCN to synthesize α-aminonitrile. The results are also summarized in Table 1 (entries 6–25). Similarly, the yields of α -aminonitriles followed the same rules as using **1a** imine, and the highest yields were achieved in the presence of Al-PKU-1 catalyst.

In theory, Al_xGa_{1-x}-PKU-1 can provide both Brønsted and Lewis acid sites, the former coming from B-OH and the latter from the electron-deficient B atoms (BO3 groups) owing to their vacant $2p_{\pi}$ orbitals. Three-fold coordinated B atoms are usually considered as an efficient Lewis acid center, for example, BF₃ was used as a strong Lewis acid in some homogeneously acidcatalyzed organic reactions.³⁵ As for Al_rGa_{1-r} -PKU-1, however, the further investigations gave the indication that BO₃ groups in the framework do not exhibit any acidic attributes. As shown in Table 2, when these as-synthesized Al_xGa_{1-x} -PKU-1 catalysts (x = 0, 0.5, 1) were preheated at high temperatures, the yields of 2a all declined dramatically. Taking Al-PKU-1 as an example, the Al-PKU-1 sample without the heating treatment gave the yield as high as 91%, however, after heating at 523 and 673 K, the yields of 2a declined to one eighth and one fifteenth of the original values. The above results agree with the destruction of Brønsted acid centers in Al_xGa_{1-x} -PKU-1. As the Brønsted acid centers, B-OH groups in the framework can effectively activate the resolved reactants in the imine cyanation, however they are forced to be released gradually in the form of H₂O during high temperature calcination; finally, the destruction of these active sites will result in a rapid decline in the catalytic activity for

Table 1 Al_xGa_{1-x} -PKU-1 (x = 0, 0.2, 0.5, 0.8, 1) catalyzed Strecker reactions using different aromatic imines



Table 2 Yields of 2a catalyzed by thermally-treated ${\sf Al}_x{\sf Ga}_{1-x}\text{-}{\sf PKU-1}$ at different temperatures

Ts—]	H 0.2 mmol 0.4 mmol	0.2 equiv. catalyst Ts- N ₂ , 45 °C, 3 h, CHCl ₃ (1 mL)	
Entry	Catalyst	Temperature (°C)	Yield (%)
1	Al-PKU-1	As-synthesized	91.0
2	Al-PKU-1	250	10.9
3	Al-PKU-1	400	6.4
4	Al-PKU-1 ^a	627	17.0
5	Al _{0.5} Ga _{0.5} -PKU-1	As-synthesized	62.0
6	Al _{0.5} Ga _{0.5} -PKU-1	250	7.4
7	Al _{0.5} Ga _{0.5} -PKU-1	400	3.6
8	Ga-PKU-1	As-synthesized	24.0
9	Ga-PKU-1	250	5.4
10	Ga-PKU-1	400	3.5
11	Ga-PKU-1 ^b	627	85.0

 a Al-PKU-1 has transformed into Al₄B₂O₉ at this temperature. b Ga-PKU-1 has transformed into Ga_4B₂O₉ at this temperature.

imine cyanation. Based on the above experimental facts, it is rationally inferred that the three-fold coordinated B atoms are unable to offer the Lewis sites to activate Strecker reactions. Probably, these small-volume B atoms are difficult to be approached efficiently by these large organic substrates owing to steric hindrance.

FT-IR spectra can also display obvious changes of vibration modes to evidence the above-mentioned dehydroxylation process. As shown in Fig. 6, at room temperature, both Ga-PKU-1 and Al-PKU-1 give a broad and strong absorption peak in the range of 3000–3800 cm⁻¹, corresponding to O–H stretching vibrations of weakly-absorbed water molecules and hydroxyl groups in the framework. After heating at 250 °C, the above absorption band tends to shrink until splitting into several independent peaks. In this process, the O–H vibration peaks originating from physically-absorbed water molecules become weaker due to the progressive escape of water molecules; in the meantime, hydroxyl groups in the framework are still thermodynamically stable and therefore their vibration modes become more visible. Namely, three independent O–H vibration peaks, located at around 3175, 3434 and 3640 cm⁻¹, appeared

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prominently after heating. Judging from the crystal microstructure, these three vibration peaks coincide with three kinds of –OH groups in the framework, *i.e.* $BO_2(OH)$, $B_2O_4(OH)$ and $BO(OH)_2$. Upon further heating to a higher temperature, Ga-PKU-1 and Al-PKU-1 will undergo a complete dehydration process to lose most of the B–OH groups, thus eventually resulting in the collapse of the framework and the disappearance of Brønsted acid sites. In addition, compared to the as-prepared PKU-1 sample, there appeared two new vibration peaks at around 2340 and 1860 cm⁻¹ at 250 °C, and these newly-emerged two vibration peaks exactly reflected the transient changes of borates or hydroxyl groups in the PKU-1 framework during the dehydroxylation process.

It is remarkable that Ga-PKU-1 and Al-PKU-1 exhibited entirely different catalytic behaviors when they were further calcined at a higher temperature. As indicated in entries 4 and 11 of Table 2, the yields of 2a showed a significant increase after a severe heat-treatment at 627 °C. In detail, when raising the temperature from 400 to 627 °C, the catalytic activity of Al-PKU-1 and Ga-PKU-1 abnormally increased by 2 and more than 20 times, respectively. In essence, although PKU-1 has completely lost its Brønsted acid sites, it was possible to restructure a large number of new Lewis acid/base sites in its framework to accelerate imine cyanation during the calcination process. As a matter of fact, the framework of Al- or Ga-PKU-1 is thermodynamically unstable at 627 °C and will transform into a mullite-type structure (Al₄B₂O₉ or Ga₄B₂O₉).³⁶ Al₄B₂O₉ and Ga₄B₂O₉ have a similar crystal structure, in which octahedral units (AlO₆ or GaO₆) share edges in a trans-manner forming one-dimensional chains along the *b*-direction, and the chains are further cross-linked into a mullite-type structure by BO₃, BO4, AlO4 and AlO5 in Al4B2O9 or BO3, BO4 and GaO5 in Ga₄B₂O₉. Theoretically, Al or Ga atoms with unsaturated coordination are potential Lewis acid sites, and organic substrates tend to bond with these unsaturated sites in the energeticallyfavored configuration to be activated. The significant increase of 2a yield using the $Ga_4B_2O_9$ catalyst is most likely from the generation of stronger basic centers, *i.e.* µ₃-O neighboring with

5-coordinated Ga³⁺; these oxygen atoms seem to act as the adsorption sites in base-catalyzed Strecker reactions.¹⁰

Reusability is an important factor to value the performance of heterogeneous catalysts, and therefore, the recycling experiments using three types of Al_xGa_{1-x} -PKU-1 catalysts (x = 0, 0.5, 1) were performed, and the heterogeneous nature of this reaction allowed the quick recovery of the solid catalyst from the solution. After each catalytic run, the powder catalyst was separated by centrifugation followed by solvent-washing. The recovered catalyst was dried and activated at 100 °C for 60 min prior to the next run. Fig. 7 reveals that no considerable activity loss for Al_xGa_{1-x} -PKU-1 catalysts (x = 0, 0.5, 1) was observed for at least 4 successive runs. The XRD pattern for the recovered catalyst (after 4 runs) also exhibited no obvious decline of crystallinity. So, Al_xGa_{1-x} -PKU-1 catalysts are stable and can maintain their framework structure under the performed reaction conditions.

Catalytic mechanisms of imine cyanations promoted by Brønsted acid sites have been discussed elsewhere.3,15 As illustrated in Fig. 8, the imine was first activated by the massive B-OH groups by protonation to produce an active imine intermediate; thereafter, TMSCN was activated by the O^{2-} site neighboring the B atom to coordinate with O²⁻ to form a 5-coordinated silicate species so that the cyanide group was polarized to acquire more reactivity. The resultant intermediate species of 5-coordinated silicate was proved elsewhere by solid state ²⁹Si MAS-NMR spectra.37,38 In the meantime, the activated imine by Brønsted acid sites was attacked by these highly reactive cyanide ions to form an N-TMS intermediate, which was subsequently hydrolyzed to other products due to the cleavage of the rather labile N-Si bond by a trace amount of moisture present in the solvent, which is very important to accelerate the transformation of the substrate, as observed earlier by Feng et al.3

Conclusion

In conclusion, complete solid solutions of Al_xGa_{1-x} -PKU-1 (x = 0, 0.2, 0.5, 0.8, 1), composed of two molecular sieves with



Fig. 7 Structural stability identified by PXRD patterns of Ga-PKI-1 (a), $Al_{0.5}Ga_{0.5}$ -PKU-1 (b), Al-PKU-1 (c) after four cycles and the reusability (d). Reaction conditions: 0.2 mmol of imines (**1a**), 0.4 mmol of TMSCN, Al_xGa_{1-x} -PKU-1 catalyst (0.2 equiv., x = 0, 0.5, 1), 1 mL of chloroform, N_2 atmosphere, 3 h. The yield was calculated according to ¹H NMR measurements.



Fig. 8 The proposed reaction mechanism of Strecker reactions over Al_xGa_{1-x} -PKU-1 solid acids.

octahedron-based frameworks (Ga-PKU-1 and Al-PKU-1), have been facilely synthesized by the molten boric acid method. The as-synthesized Al_xGa_{1-x}-PKU-1 solid acid catalysts become more efficient in the cyanation of aldimines with the increase of x. The enhancement in catalytic activity was largely contributed from the stronger Brønsted acidic strength and more Brønsted acidic sites generated with the incorporation of Al atoms, which was evidenced with the NH₃-TPD measurement. Despite their electron deficiency, boron atoms in Al_xGa_{1-x}-PKU-1 seem unable to act as Lewis acidic centers to catalytically activate Strecker reactions probably due to the steric hindrance against the approach of large organic substrates according to the fact of the severe weakening of α -aminonitrile yields after a dehydroxylation process at given temperatures. Despite the great challenges in the design and preparation of solid solutions in the field of porous materials, Al_xGa_{1-x}-PKU-1 has potentially provided an effective method and a beneficial reference to control surface acidity or basicity of porous materials.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 C. Nájera and J. M. Sansano, Chem. Rev., 2007, 107, 4584–4671.
- 2 A. G. Myers and D. W. Kung, J. Am. Chem. Soc., 1999, **121**, 10828–10829.
- 3 J. Wang, X. Liu and X. Feng, Chem. Rev., 2011, 111, 6947–6983.
- 4 D. Reinares-Fisac, L. M. Aguirre-Diaz, M. Iglesias, N. Snejko, E. Gutierrez-Puebla, M. Á. Monge and F. Gandara, *J. Am. Chem. Soc.*, 2016, **138**, 9089–9092.
- 5 L. M. Aguirre-Díaz, F. Gandara, M. Iglesias, N. Snejko,
 E. Gutiérrez-Puebla and M. Á. Monge, *J. Am. Chem. Soc.*, 2015, 137, 6132–6135.
- 6 A. Verma, K. Tomar and P. K. Bharadwaj, *Inorg. Chem.*, 2017, 56, 13629–13633.
- 7 J. Choi, H. Y. Yang, H. J. Kim and S. U. Son, Angew. Chem., Int. Ed., 2010, 49, 7718–7722.
- 8 S. Gonell, M. Poyatos and E. Peris, *Chem. Eur. J.*, 2014, **20**, 5746–5751.
- 9 F. Rajabi, S. Nourian, S. Ghiassian, A. M. Balu, M. R. Saidi, J. C. Serrano-Ruiz and R. Luque, *Green Chem.*, 2011, 13, 3282–3289.
- S. X. Hu, W. L. Wang, M. F. Yue, G. J. Wang, W. L. Gao, R. H. Cong and T. Yang, *ACS Appl. Mater. Interfaces*, 2018, 10, 15895–15904.
- B. Karmakar, A. Sinhamahapatra, A. B. Panda, J. Banerji and B. Chowdhury, *Appl. Catal.*, A, 2011, 392, 111–117.
- 12 A. K. Shah, N. H. Khan, G. Sethia, S. Saravanan, R. I. Kureshy, S. H. R. Abdi and H. C. Bajaj, *Appl. Catal.*, *A*, 2012, **419**, 22–30.
- 13 M. Shekouhy, Catal. Sci. Technol., 2012, 2, 1010-1020.
- 14 A. Mobaraki, B. Movassagh and B. Karimi, *ACS Comb. Sci.*, 2014, **16**, 352–358.
- 15 M. G. Dekamin, M. Azimoshan and L. Ramezani, *Green Chem.*, 2013, **15**, 811–820.
- 16 J. Chai, P. C. Wang, J. Jia, B. Ma, J. Sun, Y. F. Tao, P. Zhang,
 L. Wang and Y. Fan, *Polyhedron*, 2018, 141, 369–376.
- 17 D. Zareyee, A. S. Rad, Z. Ataei, S. H. Javadi and M. A. Khalilzadeh, *Appl. Organomet. Chem.*, 2018, **32**, 1–6.

- 18 N. V. Costantini, A. D. Bates, G. J. Haun, N. M. Chang and G. Moura-Letts, ACS Sustainable Chem. Eng., 2016, 4, 1906–1911.
- 19 J. C. Wang, Y. Masui and M. Onaka, *Eur. J. Org. Chem.*, 2010, 1763–1771.
- 20 J. Ju, J. H. Lin, G. B. Li, T. Yang, H. M. Li, F. H. Liao, C. K. Loong and L. P. You, *Angew. Chem., Int. Ed.*, 2003, 42, 5607–5610.
- 21 W. L. Gao, Y. Jing, J. Yang, Z. Y. Zhou, D. F. Yang, J. L. Sun, J. H. Lin, R. H. Cong and T. Yang, *Inorg. Chem.*, 2014, 53, 2364–2366.
- T. Yang, A. Bartoszewicz, J. Ju, J. L. Sun, Z. Liu, X. D. Zhou,
 Y. X. Wang, G. B. Li, F. H. Liao, B. Martin-Matute and
 J. H. Lin, *Angew. Chem., Int. Ed.*, 2011, 50, 12555–12558.
- 23 H. Chen, J. Ju, Q. P. Meng, J. Su, C. Lin, Z. Y. Zhou, G. B. Li, W. L. Wang, W. L. Gao, C. M. Zeng, C. Tang, J. H. Lin, T. Yang and J. L. Sun, *J. Am. Chem. Soc.*, 2015, 137, 7047–7050.
- 24 J. Ju, T. Yang, G. B. Li, F. H. Liao, Y. X. Wang, L. P. You and J. H. Lin, *Chem. – Eur. J.*, 2004, **10**, 3901–3906.
- 25 T. Yang, J. Ju, G. B. Li, F. H. Liao, X. D. Zhou, F. Deng, L. Chen, Y. X. Wang and J. H. Lin, *Inorg. Chem.*, 2007, 46, 4772–4774.
- 26 W. L. Gao, Y. X. Wang, G. B. Li, L. P. You and J. H. Lin, *Inorg. Chem.*, 2008, 47, 7080–7082.
- 27 W. L. Wang, S. Y. Zhang, S. X. Hu, D. Wang, W. L. Gao, R. H. Cong and T. Yang, *Appl. Catal.*, A, 2017, 542, 240–251.
- 28 W. L. Wang, S. X. Hu, L. J. Li, W. L. Gao, R. H. Cong and T. Yang, J. Catal., 2017, 352, 130–141.
- 29 G. J. Wang, W. L. Wang, F. H. Zhang, W. L. Gao, R. H. Cong and T. Yang, *Catal. Sci. Technol.*, 2016, 6, 5992–6001.
- 30 W. L. Wang, Y. Wang, B. Wu, R. H. Cong, W. L. Gao, B. Qin and T. Yang, *Catal. Commun.*, 2015, 58, 174–178.
- 31 Q. Q. Li, C. Lin, Z. Y. Zhou, J. Ju, G. B. Li, J. H. Lin, W. L. Gao, R. H. Cong and T. Yang, *Inorg. Chem.*, 2014, 53, 5600–5608.
- 32 W. L. Gao, T. Yang, Y. X. Wang, G. B. Li, F. H. Liao and J. H. Lin, J. Phys. Chem. B, 2005, 109, 22775–22779.
- 33 TOPAS V:*TOPAS, V4.1-beta*, Bruker AXS, Karlsruhe, Germany, 2004.
- 34 C. Angelici, M. E. Z. Velthoen, B. M. Weckhuysen and P. C. A. Bruijnincx, *Catal. Sci. Technol.*, 2015, 5, 2869–2879.
- 35 H. Shen, X. Xiao, M. K. Haj, P. H. Willoughby and T. R. Hoye, J. Am. Chem. Soc., 2018, 140, 15616–15620.
- 36 R. H. Cong, T. Yang, K. Li, H. M. Li, L. P. You, F. H. Liao, Y. X. Wang and J. H. Lin, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2010, 66, 141–150.
- 37 Z. Jiao, X. Feng, B. Liu, F. Chen, G. Zhang and Y. Jiang, *Eur. J. Org. Chem.*, 2003, 3818–3826.
- 38 M. L. Kantam, K. Mahendar, B. Sreedhar and B. M. Choudary, *Tetrahedron*, 2008, 64, 3351–3360.