

Cite this: *J. Mater. Chem. A*, 2025, **13**, 4292

# Organic-free synthesis of silicoaluminophosphate zeotype membranes with tunable framework charge density†

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Microporous crystalline membranes utilizing strong adsorptive affinity for separation, especially at elevated temperatures, are needed for separating mixtures containing polar and nonpolar molecules with similar sizes. Zeotype membranes with tunable framework charge densities (FCDs) may serve as a promising candidate for separating such mixtures under industrially relevant conditions. Typically, synthesis of zeotype membranes requires organic compounds as structure-directing agents (SDAs), increasing synthesis cost and complexity and thus potentially restricting their large-scale use. This work reports, for the first time, organic-free synthesis of silicoaluminophosphate (SAPO) zeotype membranes with LTA topology by secondary growth. By varying framework heteroatom (Si) concentrations, the FCD of LTA-type SAPO membranes was tuned between 0.30 and 0.37 with respect to charge-density matching with the inorganic SDA, Na<sup>+</sup> cation. Highly charged SAPO membranes showed good separation performance of ammonia (NH<sub>3</sub>) over non-polar N<sub>2</sub> and H<sub>2</sub> gases, with selectivities of 32.5 and 9.9, respectively, and excellent thermal stability over 100 h at 150 °C. This inorganic synthesis strategy might be applicable to the fabrication of other types of zeotype membranes with adjustable compositions for affinity-based separations.

Received 19th September 2024  
Accepted 20th December 2024

DOI: 10.1039/d4ta06666a

rsc.li/materials-a

## 1. Introduction

Membranes for separation under industrially relevant conditions, especially at elevated temperatures, can realize substantial energy savings.<sup>1,2</sup> Although polymers possess excellent processibility for membrane fabrication, they often suffer from a low degree of thermal stability, making them inapplicable for such separations.<sup>3</sup> Microporous inorganic materials, such as zeolites with molecular-sized pores, have exceptional thermal, mechanical and chemical stabilities and thus are promising alternatives for fabricating membranes for gas separation at high temperatures.<sup>4–8</sup>

Besides zeolites, a family of aluminophosphate (AlPO<sub>4</sub>)-based molecular sieves, including heteroatom-substituted zeotypes, such as silicoaluminophosphate (SAPO) materials, have also been utilized for membrane fabrication.<sup>9–12</sup> For example, due to their limited availability in aluminosilicate zeolite systems, AEI- and AFI-type membranes have been fabricated

from AlPO<sub>4</sub>-18 and SAPO-5 zeotype materials and demonstrated potential for CO<sub>2</sub> and hydrocarbon separations using their small- and large-pore frameworks, respectively.<sup>13–15</sup> On the other hand, zeotype membranes often exhibit enhanced separation performance compared to zeolite membranes, even if they share the same framework topology. For example, SAPO-34 membranes, analogues of CHA-type zeolite membranes, have shown higher N<sub>2</sub> permeance compared to SSZ-13 membranes, making them more attractive in N<sub>2</sub> separation for the natural gas process.<sup>16,17</sup>

However, the synthesis of zeotype membranes usually requires the use of organic structure-directing agents (SDAs), such as alkylamines or organoammonium cations, either for seed-crystal preparation and/or secondary membrane growth,<sup>8,11,12</sup> despite many efforts toward template-free or gel-free membrane growth.<sup>18–20</sup> On the other hand, in the synthesis of low-silica (Si/Al ≤ 3) zeolite membranes, a smaller metal cation with higher charge density has been used as an inorganic SDA to introduce higher framework charge density (FCD), providing enhanced adsorption selectivity for polar molecules.<sup>21,22</sup> This, therefore, arouses great interest in developing a complete inorganic synthesis strategy for the fabrication of zeotype membranes, where high-charge-density inorganic SDAs would allow the introduction of a higher FCD within zeotype membranes, realizing more effectively controlled affinity-based separations. Moreover, this would

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eliminate the energy intensive calcination step that is typically required for the synthesis of zeolitic materials using organic SDAs.

Herein, we report unprecedented organic-free synthesis of SAPO zeotype membranes using an alkali metal cation as an inorganic SDA, with relatively higher charge density compared to zeotype materials synthesized from organic SDAs. As the first analogue of commercial NaA zeolite membranes, we fabricated a series of small-pore ( $\sim 4.5$  Å) LTA-type SAPO (SAPO-LTA) membranes with highly charged frameworks whose FCD was effectively controlled by varying framework heteroatom distributions. We also demonstrated the high-temperature (up to 300 °C) application of these highly charged SAPO-LTA membranes for affinity-based separation of polar gas ( $\text{NH}_3$ ) from similarly sized, non-polar gases ( $\text{H}_2$  and  $\text{N}_2$ ).

## 2. Experimental section

### 2.1 Preparation of SAPO-LTA molecular sieves

The reagents used for the synthesis of SAPO molecular sieves as seed crystals included NaOH (50%, Aldrich), aluminium hydroxide (99%, Aldrich), phosphoric acid (85%, Merck), Ludox AS-40 (40% colloidal silica in water, Aldrich), and de-ionized (DI) water. The oxide composition of the final synthesis mixture was  $2.4\text{Na}_2\text{O} \cdot 1.0\text{Al}_2\text{O}_3 \cdot 0.9\text{P}_2\text{O}_5 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ , where  $x$  and  $y$  are varied between  $2.0 \leq x \leq 3.0$  and  $100 \leq y \leq 300$ , respectively. All chemical reagents were mixed by high-speed stirring to prepare homogeneous synthesis gels. The prepared synthesis mixtures were heated at 135 °C for 1 day. The obtained solid product was washed with DI water and dried at 70 °C.

### 2.2 Synthesis of SAPO-LTA membranes

SAPO-LTA membranes were prepared on  $\alpha\text{-Al}_2\text{O}_3$  ceramic hollow fiber supports (Media and Process Technology Inc, outer diameter: 5.7 mm, average pore size: 0.4  $\mu\text{m}$ , wall thickness: 1 mm, and length: 7 cm), *via* a hydrothermal secondary growth method.<sup>1,8</sup> The ceramic supports were first washed with DI water under sonication for 1 h. After drying the supports at 200 °C for 1 h, a tip of the cooled-down support was glazed at 1000 °C for 6 h. The one-end sealed alumina supports were then dip-coated with 2 wt% seeding solutions prepared using the synthesized SAPO-LTA seed crystals, followed by drying at 200 °C overnight. The hydrothermal secondary growth of SAPO-LTA membranes was carried out on the seeded supports using SAPO synthesis mixtures identical to those used for the corresponding seed crystal synthesis, at 135 °C for 1 day. The as-synthesized membranes were recovered after washing several times with DI water and dried for up to 24 h at room temperature.

### 2.3 Characterization of LTA-type SAPO seed crystals and SAPO-LTA membranes

The crystal topologies and crystallinity of the LTA-type SAPO materials were determined by powder X-ray diffraction (XRD) on a Rigaku Ultima IV diffractometer with Cu K $\alpha$  radiation at 40 kV and 40 mA. Crystal morphologies and sizes were determined by

Carl Zeiss AURIGA CrossBeam field-emission scanning electron microscopy (SEM). The cross-sectional thickness was determined using energy dispersive spectroscopy (EDS) using a Hitachi SU70 FESEM coupled with an Oxford EDS. The crystal size distributions of SAPO-LTA in the seeding solution were determined by dynamic light scattering (DLS, Malvern Panalytical Zetasizer Nano). Elemental analysis for Na, Al, P and Si of the seed crystals was conducted using a Jarrell-Ash Polyscan 61E inductively coupled plasma spectrometer in combination with a PerkinElmer 5000 atomic absorption spectrophotometer. Thermogravimetric and differential thermal analyses (TGA/DTA) were performed in air on a TA Instruments SDT 2960 thermal analyser at a heating rate of 5 °C min<sup>-1</sup>. <sup>29</sup>Si Magic-Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) measurements were performed on a Bruker DRX500 spectrometer at a spinning rate of 20.0 kHz. The <sup>29</sup>Si MAS NMR spectra were recorded at a <sup>29</sup>Si frequency of 99.362 MHz with a  $\pi/2$  rad pulse length of 4.0  $\mu\text{s}$ , a recycle delay of 10 s, and an acquisition of about 5000 pulse transients. The <sup>29</sup>Si chemical shifts are referenced to TMS. <sup>27</sup>Al and <sup>31</sup>P MAS NMR measurements were also performed on a DRX500 spectrometer at a spinning rate of 21.0 kHz. The solid sample was dehydrated at 250 °C for 6 h under a dynamic vacuum of  $10^{-3}$  torr. <sup>27</sup>Al and <sup>31</sup>P MAS NMR data were collected at 130 and 202 MHz with a  $\pi/6$  rad pulse length of 1.0 and 3.0  $\mu\text{s}$ , respectively. The <sup>27</sup>Al and <sup>31</sup>P chemical shifts are referenced to an  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  solution and a  $\text{H}_3\text{PO}_4$  solution, respectively.  $\text{N}_2$  gas adsorption measurements at 77 K were conducted using a Micromeritics 3Flex system.  $\text{NH}_3$  temperature-programmed desorption ( $\text{NH}_3$ -TPD) was performed on a flow-type, fixed bed apparatus combined with a mass spectrometer (OmniStar GSD 350, Pfeiffer Vacuum). 0.1 g of SAPO-LTA seed crystals were activated in flowing  $\text{N}_2$  (50 sccm) at 250 °C for 4 h. Then,  $\text{NH}_3$  was flowed over the samples at 150 °C for 30 minutes. Finally,  $\text{NH}_3$ -TPD was performed in flowing  $\text{N}_2$  (20 sccm) from 150 to 700 °C with a temperature ramping rate of 10 °C min<sup>-1</sup>. The detailed information on the material preparation and gas separation methods is available in the ESI.<sup>†</sup>

## 3. Results and discussion

The synthesis procedure of SAPO-LTA membranes is illustrated in Fig. 1. To fabricate SAPO membranes by seeded growth under entirely inorganic conditions, we first prepared sodium-SAPO synthesis gels that can be used for both seed-crystal synthesis and membrane growth. By using the gels with adjusted Si contents, SAPO-LTA crystals with varied FCD were synthesized as seed crystals. Subsequently, porous alumina supports (Fig. S1<sup>†</sup>, OD: 5.7 mm; pore size: 400 nm) were seeded by a dip-coating process with each crystal. After that, secondary growth of SAPO-LTA membranes on the seeded supports was conducted using the gels under the optimized crystallization conditions that can also yield the SAPO seed crystals, to effectively control the chemical compositions of the resulting membranes with FCD corresponding to those of the seeds.

Because the secondary growth of zeolitic membranes involves seeded crystallization along a thin layer of targeted





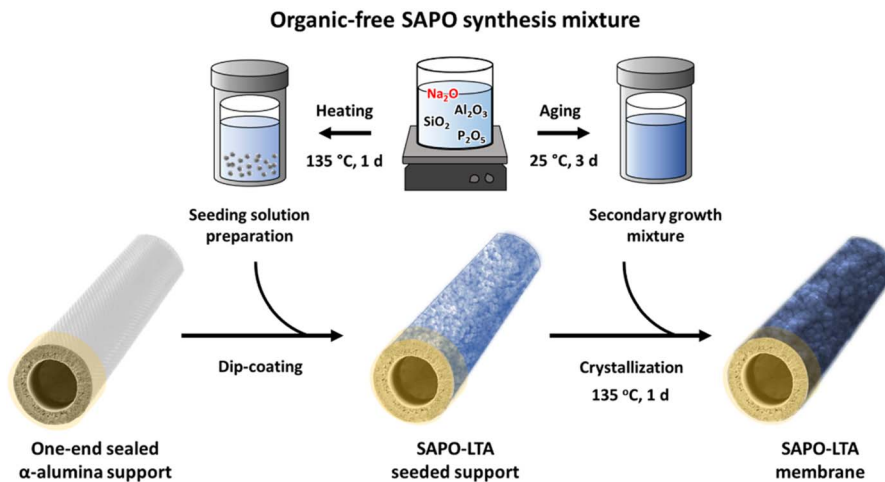


Fig. 1 Schematic illustration of the synthesis procedure for organic-free SAPO-LTA membranes via secondary growth.

zeolite seeds, a uniform deposition of nano-sized seed crystals on the substrate is required to improve the resulting membrane quality.<sup>6–8</sup> Therefore, our initial attempt at SAPO-LTA membrane fabrication was made with the synthesis of SAPO-LTA crystals of such small sizes (Table S1†). According to the previously known synthesis system for organic-free Na-SAPO-LTA molecular sieves,<sup>23</sup> indeed, we were only able to obtain micron-sized SAPO-LTA crystals ( $\geq 1 \mu\text{m}$ ) from Na-SAPO gels with the composition of  $2.4\text{Na}_2\text{O} \cdot 1.0\text{Al}_2\text{O}_3 \cdot 0.9\text{P}_2\text{O}_5 \cdot (2.0\text{--}2.5)\text{SiO}_2 \cdot 100\text{H}_2\text{O}$  (Fig. S2†). However, when the gels with a wider

range of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios ( $x = 2.0\text{--}3.0$ ) were further diluted ( $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 = 300$ ), we could synthesize phase-pure LTA-type SAPO crystals (denoted as SAPO-LTA- $x$ ) (Fig. 2a) as small as  $\sim 500 \text{ nm}$  (Fig. 2b and S2†), with the aid of a small addition (4 wt%  $\text{Al}_2\text{O}_3$ ) of the micron-sized SAPO-LTA into the diluted gels (Table S1†). In fact, a crystallization time of 1 day at  $135^\circ\text{C}$  for the synthesis of nano-sized SAPO-LTA as seed crystals was carefully selected for the maximum crystallinity of products observed from the crystallization kinetics (Fig. S3†). This further allowed us to determine secondary membrane

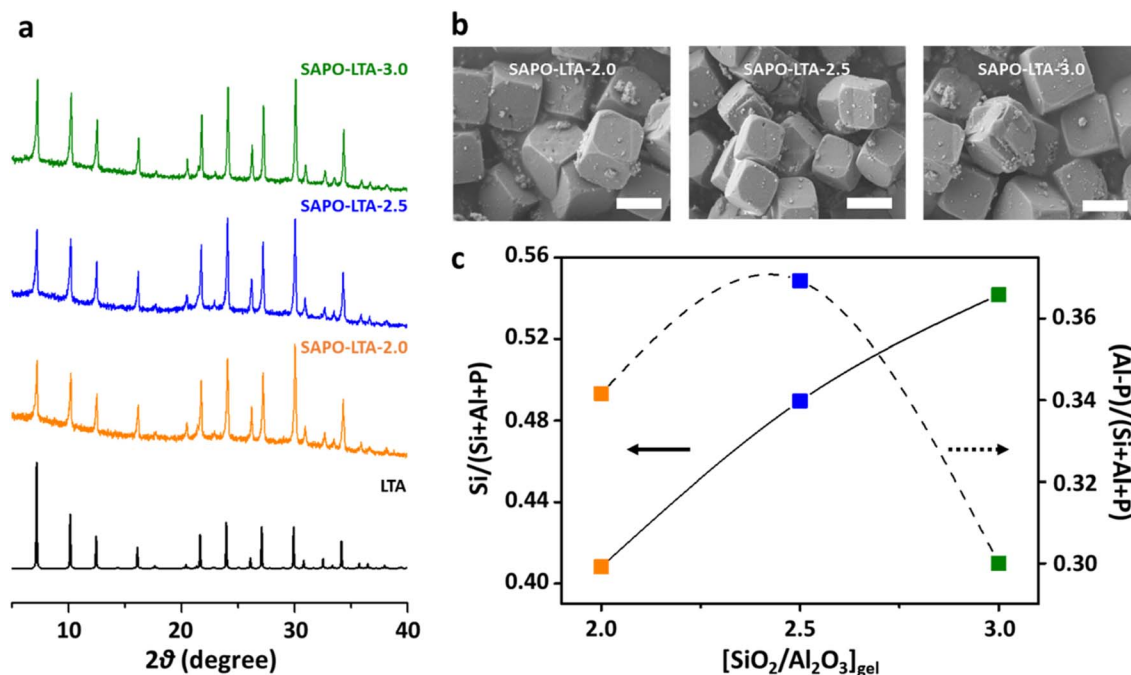


Fig. 2 Characterization of organic-free SAPO-LTA crystals with sub-micron sizes. (a) Powder XRD patterns of SAPO-LTA crystals prepared from synthesis gels with three different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (i.e., 2.0, 2.5 and 3.0), which are in good agreement with the theoretical LTA pattern (bottom).<sup>13</sup> (b) SEM images (scale bar: 500 nm) of the SAPO-LTA crystals. (c) Framework chemical compositions of the SAPO-LTA crystals.  $\text{Si}/(\text{Si} + \text{Al} + \text{P})$  and  $(\text{Al}-\text{P})/(\text{Si} + \text{Al} + \text{P})$  indicate their framework Si fraction and FCD, respectively.





crystallization conditions (*i.e.*, 135 °C for 1 day) using the same SAPO gel that was already optimized for the seed synthesis.

The chemical compositions of three different SAPO-LTA crystals (size:  $\sim 500$  nm) were determined by elemental and thermal analyses (Table S2 and Fig. S4†). The framework Si fraction of the SAPO materials, *i.e.*,  $\text{Si}/(\text{Si} + \text{Al} + \text{P})$ , increased with respect to the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the gels. However, SAPO-LTA-2.5 possessed the highest FCD (the fraction of Si atoms carrying the actual charges compensated by extra-framework  $\text{Na}^+$  cations;  $(\text{Al}-\text{P})/(\text{Si} + \text{Al} + \text{P}) = 0.37$ ), among the SAPO-LTA crystals, despite its lower Si fraction (0.49) compared to SAPO-LTA-3.0 (0.54), as shown in Fig. 2c. This is probably due to more isomorphous Si substitution for Al-P pairs according to the known Si substitution mechanism (SM) II during the crystallization, leading to the formation of a larger siliceous area within SAPO-LTA-3.0 compared to SAPO-LTA-2.5, as further evidenced by  $^{29}\text{Si}$  MAS NMR spectroscopy (Fig. S5†).<sup>24,25</sup> The most abundant presence of  $^{29}\text{Si}$  NMR resonances in the region below  $-90$  ppm, assignable to the framework  $\text{Si}(\text{OAl})_n$  species ( $n = 3-0$ ) in SAPO-LTA-3.0, indicated that its highest Si fraction rather resulted in the lowest FCD, according to charge-density matching between the anionic framework and extra-framework  $\text{Na}^+$  cations.<sup>26,27</sup> This is further evidenced by the proportional decrease in the number of extra-framework  $\text{Na}^+$  cations per unit cell as the FCD of SAPO materials decreases (Table S2†).

Accordingly, the highest  $\text{Na}^+$  concentration observed in SAPO-LTA-2.5 can be attributed to the preferential substitution of P by Si atoms over Al-P pairs (following SM I),<sup>24,25</sup> resulting in a larger number of negatively charged Si atoms per unit cell (FCD).

$^{27}\text{Al}$  MAS NMR spectra of all SAPO-LTA materials are characterized by a predominant resonance at 62 ppm with a small shoulder in the upfield range (30–50 ppm), assignable to tetrahedrally coordinated framework Al species under Si-rich and P-rich environments, respectively.<sup>28</sup> For example, SAPO-LTA-2.0 with the lowest Si fraction shows a notable presence of the  $^{27}\text{Al}$  resonance at a lower chemical shift. Like the cases of other zeotype materials,<sup>23,26,28</sup> the  $^{31}\text{P}$  MAS NMR spectra of our SAPO materials also show intense and sharp resonances around  $-20$  ppm, indicating that most of the P atoms are also incorporated into frameworks together with Al and Si species, resulting in the successful crystallization of SAPO molecular sieves (Table S2 and Fig. S5†).

Using both SAPO-LTA crystals with different FCDs as seeds and their synthesis mixtures as secondary membrane growth media, we finally prepared SAPO-LTA-*x* membranes (where *x* is the gel  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio = 2.0, 2.5 or 3.0) with a typical thickness of  $\sim 20$   $\mu\text{m}$  (Fig. 3a and S6†). The chemical compositions of solid products obtained together with the membranes from their secondary growth mixtures further supported that the FCD of

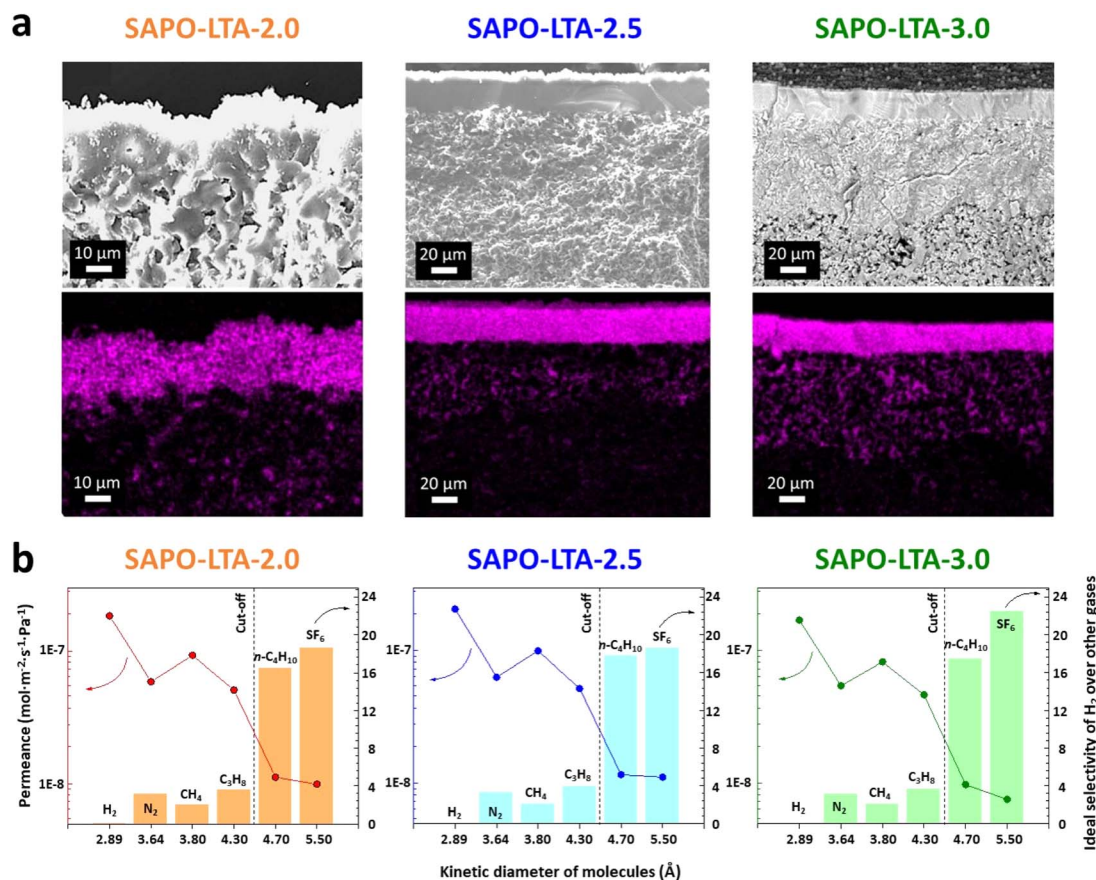


Fig. 3 SEM images and single-gas permeation of SAPO-LTA membranes. (a) SEM (top) and energy dispersive spectroscopy (bottom, Si: pink) images of SAPO-LTA membranes prepared in this work. (b) The single-gas permeance of molecules with varied kinetic diameters.





the prepared membranes was highly likely tuned to correspond to those of the seed crystals employed in their fabrication (Table S3†).

To probe the pore sizes of our SAPO-LTA membranes, the single-gas permeation of molecules with different kinetic diameters from 2.89 to 5.50 Å was evaluated at room temperature, as shown in Fig. 3b, using a home-built dead-ended permeation system (Fig. S7†). Although it was observed that N<sub>2</sub> (3.64 Å) was not readily adsorbed on SAPO-LTA crystals at 77 K like the other Na<sup>+</sup> forms of zeolite LTA (Table S2†),<sup>29,30</sup> the gas molecules smaller than 4.4 Å showed a relatively small and gradual decrease for all membranes, with a permeance of 0.5–2.0 × 10<sup>−7</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>. However, a significant decrease in gas permeance was observed for the molecules larger than 4.6 Å, exhibiting a sharp permeance cut-off between propane and *n*-butane. Although the permeation of the large molecules was not completely inhibited, indicating the inevitable presence of a few inter-crystalline defects, the notable changes between the ideal selectivity (ratio of pure gas permeances) of H<sub>2</sub> over propane and *n*-butane indicated that the effective pore size of our membranes was likely ~4.5 Å, which is slightly larger than that (~4 Å) of the LTA-type AlPO<sub>4</sub> membrane.<sup>31</sup> This is probably due to the presence of longer Si–O bonds (bond length = 1.6 Å) in the SAPO frameworks that substituted shorter P–O bonds (1.5 Å) of the LTA-type AlPO<sub>4</sub> network, like the case of a SAPO-34 membrane with high Si incorporation.<sup>16,32</sup>

Of particular interest, a polar molecule, NH<sub>3</sub>, showed considerably lower permeance at room temperature for our small-pore SAPO membranes, compared not only to non-polar H<sub>2</sub> of similar size, but also to N<sub>2</sub>, which is even heavier than NH<sub>3</sub> (Fig. S8†). Moreover, the NH<sub>3</sub> permeance was found to be lower for the membrane with higher FCD. For example, the SAPO-LTA-2.5 membrane with the highest FCD of 0.37 had the lowest NH<sub>3</sub> permeance of 0.24 × 10<sup>−7</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>, while the SAPO-LTA-3.0 membrane with the lowest FCD showed about two times higher NH<sub>3</sub> permeance (0.43 × 10<sup>−7</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>). This suggests that the extent of NH<sub>3</sub> adsorption that may impede its diffusion through the small-pore membranes can be varied with respect to the FCD of membranes that determines their overall polar properties.

Subsequently, the effect of membrane FCD on the NH<sub>3</sub> separation from a mixture of NH<sub>3</sub>/N<sub>2</sub>/H<sub>2</sub> (molar ratio of 10.0 : 22.5 : 67.5) was further investigated at an elevated temperature of 150 °C, using a Wicke–Kallenbach system (Fig. S9†). The mixture composition is representative of a product stream of the Harber–Bosch process.<sup>33,34</sup> Although it was only 10 mol% in the mixture, the presence of NH<sub>3</sub> in the mixture sufficiently lowered the permeance of both N<sub>2</sub> and H<sub>2</sub>, which otherwise had higher single-gas permeances (Fig. 4). Indeed, despite the exothermic nature of adsorption that often lowers the selectivity of membranes relying on preferential sorption in separation at elevated temperatures, the SAPO-LTA membranes showed effective NH<sub>3</sub> selectivity at this high temperature. Particularly, the SAPO-LTA-2.5 membrane exhibited a stronger NH<sub>3</sub> affinity, evidenced by the highest NH<sub>3</sub>/N<sub>2</sub> and NH<sub>3</sub>/H<sub>2</sub> selectivity (32.5 and 9.9, respectively), compared to other SAPO-LTA membranes having lower FCDs. Further, the NH<sub>3</sub> permeance (0.56 × 10<sup>−7</sup>

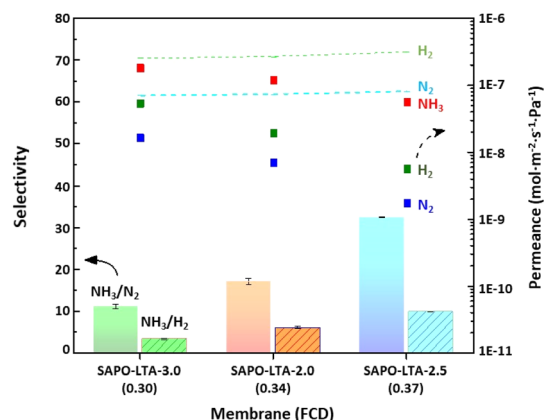


Fig. 4 Adsorption-dependent separation of NH<sub>3</sub> at 150 °C using SAPO-LTA membranes with different FCDs. The NH<sub>3</sub> selectivity (bar) over N<sub>2</sub> (left) and H<sub>2</sub> (right) of the SAPO-LTA membranes is shown with respect to their FCD. The mixture-gas permeances (symbol: ■, color code: NH<sub>3</sub>, red; H<sub>2</sub>, olive; N<sub>2</sub>, blue) are compared with the single-gas permeances (dashed line, color code: H<sub>2</sub>, green; N<sub>2</sub>, cyan) at 150 °C.

mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup>) of SAPO-LTA-2.5 was comparable to that of the other LTA-type zeolite membranes that are ~4 times thinner (Table S4†).<sup>33,34</sup> As expected, the SAPO-LTA-3.0 membrane showed the highest NH<sub>3</sub> permeance, as its weaker NH<sub>3</sub> affinity allowed a faster transport of NH<sub>3</sub> but failed to considerably block the permeance of the non-polar gases, resulting in the lowest NH<sub>3</sub> selectivity. Even at 300 °C, the SAPO-LTA-2.5 membrane maintained an adequate NH<sub>3</sub> separation performance with an NH<sub>3</sub>/N<sub>2</sub> selectivity of 14.3 and NH<sub>3</sub> permeance of 0.49 × 10<sup>−7</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup> (Fig. S10†). It is reported that to achieve *in situ* NH<sub>3</sub> removal in membrane reactors during NH<sub>3</sub> synthesis, a membrane with NH<sub>3</sub>/N<sub>2</sub> selectivity >10 and NH<sub>3</sub> permeance >0.4 × 10<sup>−7</sup> mol m<sup>−2</sup> s<sup>−1</sup> Pa<sup>−1</sup> at 300 °C is required to make the NH<sub>3</sub> synthesis membrane reactor more economical compared to traditional reactors.<sup>35</sup> Indeed, our SAPO-LTA-2.5 membrane meets these criteria.

Despite the fact that the extra-framework Na<sup>+</sup> cations are the predominant, if not the only, weak Lewis acid (LA) sites for NH<sub>3</sub> chemisorption within our organic-free SAPO materials,<sup>36–39</sup> NH<sub>3</sub>-TPD profiles demonstrate that NH<sub>3</sub> can be effectively adsorbed on the SAPO materials up to 300 °C (Fig. S11†). The primary desorption peak consistently observed around 250 °C from SAPO-LTAs further supports the lack of strong Brønsted acid sites, such as bridging hydroxyl (Si–OH–Al) groups.<sup>36,39</sup> This observation also indicates that the LA strength of our LTA-type SAPO materials is nearly similar. However, the different NH<sub>3</sub> affinities observed in SAPO-LTA membranes are not correlated with LA strength, nor are they strictly correlated with the heat of adsorption (Fig. S12†). Interestingly, the total amount of NH<sub>3</sub> desorbed, derived from the NH<sub>3</sub>-TPD desorption area, was found to be 20% and 11% larger for SAPO-LTA-2.5 (1.38 mmol g<sup>−1</sup>) compared to SAPO-LTA-3.0 (1.15) and SAPO-LTA-2.0 (1.24), respectively, closely proportional to the difference in their FCDs. Given that the LA density differentiating the overall acidity of our SAPO materials essentially corresponds to the number of Na<sup>+</sup> cations per unit cell (Table S2†), the highest NH<sub>3</sub>





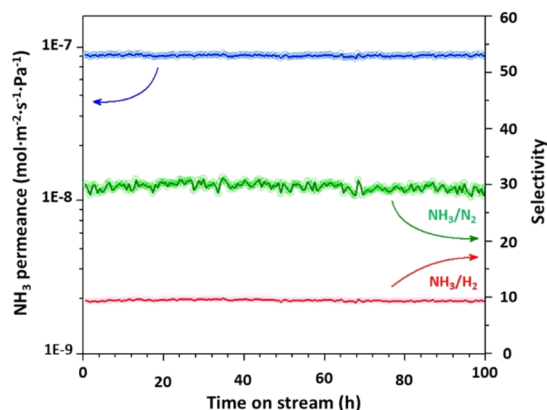


Fig. 5 A long-term (>100 h) thermal stability (at 150 °C) testing result of the SAPO-LTA-2.5 membrane for NH<sub>3</sub> separation.

affinity observed from the SAPO-LTA-2.5 membrane can be rationalized by its highest FCD.

We envision the use of SAPO-LTA membranes for the separation of NH<sub>3</sub> from unreacted N<sub>2</sub> and H<sub>2</sub> coming out of the NH<sub>3</sub> synthesis reactor at high temperatures. Since SAPO-LTA membranes can separate NH<sub>3</sub> from the mixture at high temperature, a hot retentate gas stream rich in N<sub>2</sub> and H<sub>2</sub> can be recycled back to the reactor, eliminating the need for reheating them (Fig. S13†). Indeed, to be a promising candidate for such an industrial application, membranes require long-term stability. The SAPO-LTA-2.5 membrane with the highest NH<sub>3</sub>/N<sub>2</sub> selectivity at 150 °C showed excellent long-term (>100 h) thermal stability with a fluctuation of less than 5% in NH<sub>3</sub> separation performance (Fig. 5). These SAPO-LTA membranes are among the highest performing zeolite membranes that are reported for this challenging NH<sub>3</sub> separation at high temperatures (>100 °C) (Table S4†). With the opportunity to further optimize the synthesis toward thinner membranes, it would also be possible to boost the performance of organic-free SAPO membranes for other preferential adsorbent-mediated separations at elevated temperatures.

## 4. Conclusions

In summary, we have successfully synthesized small-pore LTA-type SAPO membranes with tunable FCD without the use of organic components. By employing Na<sup>+</sup> cations as an inorganic SDA in diluted SAPO synthesis mixtures with varied Si concentrations, SAPO-LTA molecular sieves with subtly adjusted FCD were prepared as seed crystals. The use of the optimized seed-synthesis mixtures as secondary membrane growth media allowed the fabrication of small-pore (~4.5 Å) SAPO-LTA membranes with tunable FCD corresponding to that of each seed crystal employed. Among the prepared membranes, that with the highest FCD and thus with the largest number of LA sites (*i.e.*, Na<sup>+</sup> cations) per unit cell demonstrated the highest NH<sub>3</sub> selectivity over N<sub>2</sub> (32.5) and H<sub>2</sub> (9.9) over 100 h at 150 °C, with an NH<sub>3</sub> permeance of  $0.56 \times 10^{-7}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>. The organic-free synthesis strategy presented in this work might

also allow the fabrication of different types of zeotype membranes with highly charged frameworks for affinity-based separations at elevated temperatures.

## Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

## Author contribution

S. H. P.: conceptualization, methodology, investigation, writing – original draft and writing – review & editing. B. S.: methodology, investigation, writing – original draft and writing – review & editing. S. E. G.: formal analysis. K. F.: investigations and formal analysis. R. L.: methodology. A. F. M. I.: investigation and formal analysis. M. Y.: supervision, funding acquisition, project administration, writing – original draft and writing – review & editing.

## Conflicts of interest

The authors declare no conflicts of interest.

## Acknowledgements

We thank the Advanced Research Projects Agency-Energy (ARPA-E) of Department of Energy (DOE) for the financial support under the contract of DE-AR0001479.

## Notes and references

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