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## COMMUNICATION

## High-performance ammonia-selective MFI nanosheet membranes

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**Nanosheet-based MFI membranes, known to be highly selective for hydrocarbon isomer separations, exhibit NH<sub>3</sub>/N<sub>2</sub> mixture separation factor of ca. 2,236 with NH<sub>3</sub> permeance of 1.1 × 10<sup>-6</sup> mol/(m<sup>2</sup>.s.Pa), and NH<sub>3</sub>/H<sub>2</sub> separation factor of ca. 307 with NH<sub>3</sub> permeance of 2.3 × 10<sup>-6</sup> mol/(m<sup>2</sup>.s.Pa) at room temperature. Consistent with a competitive sorption-based separation, lower operating temperatures and higher pressures result in increased separation factor. At 323K, with an equimolar mixed feed of NH<sub>3</sub>/N<sub>2</sub>, the fluxes and separation factors at 3 and 7 bar are: 0.13 mol/(m<sup>2</sup>.s) and 191, and 0.26 mol/(m<sup>2</sup>.s) and 220, respectively. This performance compares favorably with that of other membranes and suggests that MFI membranes can be used in separation and purification processes involving mixtures of NH<sub>3</sub>/N<sub>2</sub>/H<sub>2</sub> encountered in ammonia synthesis and utilization. The membranes also exhibit high performance for the separation of ethane, *n*-propane and *n*-butane from H<sub>2</sub>.**

Various types of membranes, including liquid (for high temperature operation)<sup>1-3</sup> and polymeric<sup>4-11</sup> membranes have been explored as potential contributors to energy efficient processes for ammonia separation. However, liquid membranes suffer from structural instabilities, and polymeric membranes from the decline of performance at industrially relevant high-pressure and temperature conditions. Alternatively, silica<sup>12,13</sup> and zeolite<sup>12</sup> membranes have also been proposed for this application, but the reported combinations of permeances and selectivities are not sufficient for practical applications. In ref.<sup>12</sup>, the highest zeolite membrane separation factor obtained for NH<sub>3</sub>/H<sub>2</sub> separation was ca. 10, with a NH<sub>3</sub> permeance of 2.1 × 10<sup>-7</sup> mol/(m<sup>2</sup>.s.Pa) at 80 °C. Silica membranes showed a higher permeance (7.6 × 10<sup>-7</sup> mol/(m<sup>2</sup>.s.Pa)) but even lower selectivity (ca. 7). Kanezashi et al.<sup>13</sup> reported a silica

membrane with a NH<sub>3</sub> permeance of 1.0 × 10<sup>-7</sup> mol/(m<sup>2</sup>.s.Pa) and a NH<sub>3</sub>/H<sub>2</sub> separation factor of ca. 30 at 50 °C.

Recently, by using directly synthesized high-aspect-ratio zeolite MFI nanosheets, ultra-selective MFI membranes with unprecedented permeances and separation factors for *para*-xylene/*ortho*-xylene were obtained using secondary growth<sup>14,15</sup>. Herein, we report that these thin, oriented, and large-grain zeolite MFI membranes exhibit outstanding performance for the separation of ammonia from hydrogen and nitrogen. The membranes are also evaluated for the separation of hydrocarbons from hydrogen.

A well-intergrown zeolite MFI membrane, as confirmed by a high separation performance for an equimolar binary mixture of *para*-/*ortho*-xylene (i.e., a *para*-xylene permeance of 2.3 × 10<sup>-7</sup> mol/(m<sup>2</sup>.s.Pa) and a separation factor of >3000 at 150 °C and 1 kPa equimolar *para*-/*ortho*-xylene feed), is used to evaluate the performance for the separation of ammonia and hydrogen or nitrogen. Typical surface morphology and cross-sectional FIB-SEM image of the fabricated MFI membrane is shown in Figure 1S, ESI†, and is consistent with those reported in previous report<sup>15</sup>. The same membrane is used for all reported NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/N<sub>2</sub> experiments herein. Figure 1a (and Table S1, ESI†) shows the NH<sub>3</sub>/H<sub>2</sub> binary mixture separation performance at different temperatures. Permeation measurements are performed using an equimolar NH<sub>3</sub>/H<sub>2</sub> mixture feed at 3 bar while the permeate is kept at 1 bar. No sweep gas is used in the permeate side in an effort to mimic conditions that would be encountered in an actual separation process. At room temperature, the membrane exhibits a NH<sub>3</sub>/H<sub>2</sub> mixture separation factor of ca. 307 with a NH<sub>3</sub> permeance of 2.3 × 10<sup>-6</sup> mol/(m<sup>2</sup>.s.Pa), which corresponds to a flux of 0.09 mol/(m<sup>2</sup>.s). This indicates that the membrane achieves a 99.6% NH<sub>3</sub> purity in the permeate from the equimolar mixture of NH<sub>3</sub>/H<sub>2</sub> feed. The mixture separation factor, at the same feed and permeate pressures, drops drastically when the temperature increases; it is 23.8 at 50 °C and 3.8 at 100 °C. A similar trend for the separation performance is observed for the NH<sub>3</sub>/N<sub>2</sub> separation, as shown in Figure 1b and Table S2, ESI†. The membrane exhibits a NH<sub>3</sub>/N<sub>2</sub> mixture separation factor of ca. 2,236 at room temperature with a NH<sub>3</sub> permeance of 1.1 × 10<sup>-6</sup> mol/(m<sup>2</sup>.s.Pa), which corresponds to a flux of 0.07 mol/(m<sup>2</sup>.s). The separation factor drops to 191 at 50 °C and 16 at 100 °C. Figure 1e and Figure 1f compare the MFI membrane separation factor and NH<sub>3</sub> flux with literature reported values for

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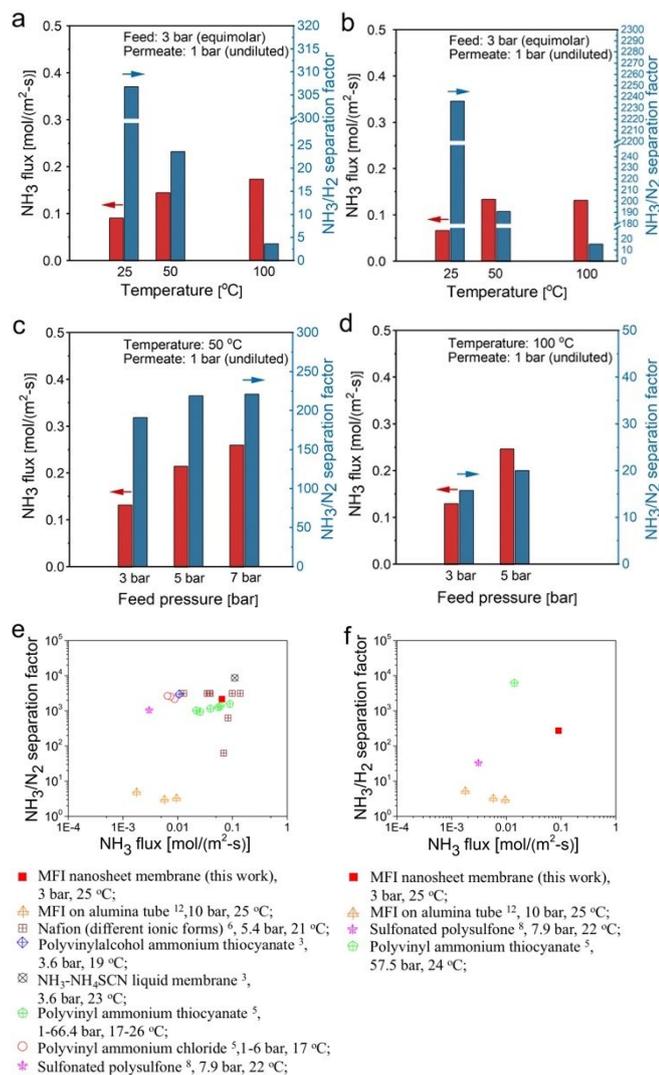
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<sup>f</sup> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



**Figure 1.** Membrane separation performance for NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/N<sub>2</sub>. NH<sub>3</sub> fluxes and mixture separation factors obtained using an equimolar NH<sub>3</sub>/H<sub>2</sub> (a) and NH<sub>3</sub>/N<sub>2</sub> (b) feed at different temperatures (25, 50 and 100 °C) with fixed feed pressure of 3 bar. NH<sub>3</sub>/N<sub>2</sub> separation performance at 50 °C (c) and 100 °C (d) with different feed pressures. In all cases, feed flow rate: 400 mL(STP)/min; no sweep gas used (i.e., non-diluted permeate); permeate pressure: 1 bar. Comparison of NH<sub>3</sub>/H<sub>2</sub> (e) and NH<sub>3</sub>/N<sub>2</sub> (f) separation performance (separation factor vs. NH<sub>3</sub> flux) for the membranes reported here and representative data from the literature (ref. <sup>3,5,6,8,12</sup>, see Appendix S1-S4, ESI<sup>†</sup>).

NH<sub>3</sub>/H<sub>2</sub> and NH<sub>3</sub>/N<sub>2</sub> separation at/near room temperature, respectively. Compared with other membranes, the nanosheet-based MFI membrane exhibits a desirable combination of high flux and separation factor. This opens the possibility for industrial NH<sub>3</sub>/H<sub>2</sub>/N<sub>2</sub> separation applications.

The high membrane separation factor towards ammonia at room temperature can be explained by the preferred adsorption of ammonia over hydrogen or nitrogen. Based on reported adsorption isotherms of NH<sub>3</sub> in pure silica MFI <sup>16</sup>, at 298 K and 3 bar (1.5 bar NH<sub>3</sub>), MFI pores are occupied by NH<sub>3</sub> at a loading of 2.6 mol/kg, which is high when compared with the saturation capacity (ca. 4.3

mol/kg). The preferred adsorption of NH<sub>3</sub> in the zeolite pores can hinder or block the flow of hydrogen or nitrogen, thus resulting in a high membrane separation factor towards ammonia. At higher temperatures, the loading of NH<sub>3</sub> in MFI pores is decreased, resulting in a drastic decrease of the membrane separation factor.

Using the NH<sub>3</sub> isotherms reported in ref. <sup>16</sup> and the NH<sub>3</sub> diffusivities reported by Jobic et al. <sup>17</sup>, which range from  $6 \times 10^{-11}$  to  $10^{-9}$  m<sup>2</sup>/s and are reported to increase with loading due to the presence of immobile and mobile adsorbed NH<sub>3</sub>, we can estimate (see ESI<sup>†</sup>) that the expected NH<sub>3</sub> flux at 25 °C with a feed pressure of 1.5 bar and permeate pressure of 1 bar ranges from 0.03 to 0.47 mol/(m<sup>2</sup>·s), which is in good agreement with the experimentally obtained values of 0.07 to 0.09 mol/(m<sup>2</sup>·s).

We have also tested the effect of pressure on the membrane separation performance using NH<sub>3</sub>/N<sub>2</sub> equimolar feed. Figures 1c and 1d (Table S2, ESI<sup>†</sup>) show NH<sub>3</sub> fluxes at various feed pressures and 1 bar undiluted permeate at fixed temperature of 50 and 100 °C, respectively. By increasing the feed pressure, NH<sub>3</sub> flux and separation factor increase. The increase in flux at high feed pressures is due to the higher driving force at higher transmembrane pressure differences. The increase in membrane separation factor can also be explained by the fractional loading of NH<sub>3</sub> in zeolite pores; at higher pressures, higher NH<sub>3</sub> loadings diminish the transport of nitrogen. At this time, we could not investigate higher pressures due to safety considerations in our system. It would be important to determine the separation performance of MFI membranes at or near the NH<sub>3</sub> saturation loading at the corresponding testing temperatures. Higher pressures and temperatures than the ones investigated here will be of interest for certain practical applications <sup>18</sup>.

The competitive adsorption separation mechanism responsible for the observed NH<sub>3</sub>/N<sub>2</sub> and NH<sub>3</sub>/H<sub>2</sub> selectivity, is well established for the separation of larger and heavier hydrocarbons from lighter gases like hydrogen <sup>19-21</sup>, nitrogen <sup>22</sup> and methane <sup>23-27</sup>. Although the novel finding of this report is the aforementioned NH<sub>3</sub> selective performance, we also report on the separation of H<sub>2</sub> and hydrocarbon mixtures, which we can compare with the corresponding reported performance of other MFI membranes. Figure 2 shows the membrane separation performance of binary (Figure 2a) and ternary (Figure 2b) H<sub>2</sub> and various hydrocarbon (i.e. ethane, *n*-propane and *n*-butane) mixtures at room temperature and atmospheric pressure on both feed and permeate sides (Ar is used as permeate sweep gas). The data are listed in Table S3 and S4, ESI<sup>†</sup>. The membrane rejects hydrogen in the presence of hydrocarbons at room temperature. With decreasing hydrocarbon molecular weight, the permeance increases slightly. As expected, *n*-butane results in a higher H<sub>2</sub>/hydrocarbon separation factor (ca. 60) compared to H<sub>2</sub>/*n*-propane (ca. 40) and H<sub>2</sub>/ethane (ca. 6). This finding agrees with the reported trend of light alkanes adsorption isotherms in silicalite-1 <sup>28</sup> and reported permeation data <sup>19-27</sup> (Appendix S5, ESI<sup>†</sup>). As the hydrocarbon loading increases with pressure, the separation factor is also expected to increase. Indeed, Figure 2c shows an increase of separation factor with increasing feed pressure for H<sub>2</sub>/*n*-butane mixture at low *n*-butane concentration (2 mol%). Figure 2d shows membrane permeation tests with equimolar H<sub>2</sub> and *n*-propane binary mixture at room temperature and higher feed pressures. By increasing the feed pressure, the membrane shows improved separation factor from ca. 30 to 80.

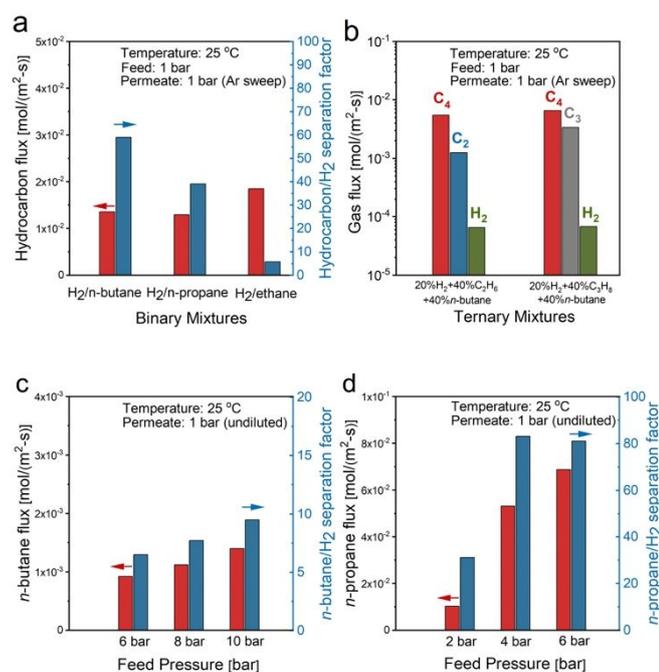


Figure 2. Membrane separation performance for  $C_2$ - $C_4$  hydrocarbons/ $H_2$  at room temperature. a) performance for binary  $H_2$  (30%)/various hydrocarbon (70%) (i.e. ethane,  $n$ -propane and  $n$ -butane) mixtures; b) Flux of components of 20% $H_2$ -40%ethane-40% $n$ -butane and 20% $H_2$ -40% $n$ -propane-40% $n$ -butane ternary mixtures; in both a) and b), feed flow rate: 50 mL(STP)/min; feed pressure: 1 bar; sweep (argon) flow rate: 30 mL(STP)/min; permeate pressure: 1 bar; c) performance for  $H_2$ / $n$ -butane mixture with a low  $n$ -butane concentration (2 mole%) at higher feed pressures; and d) membrane separation performance of equimolar  $H_2$  and  $n$ -propane binary mixture at higher feed pressures; in both c) and d), feed flow rate: 200 mL(STP)/min; permeate pressure: 1 bar; no sweep gas used (pure non-diluted permeate).

## Conclusions

Zeolite MFI membranes are fabricated from directly-synthesized nanosheets and tested for  $NH_3/H_2$ ,  $NH_3/N_2$ , and  $H_2$ /hydrocarbons separations at different temperatures and pressures. The membranes exhibit high separation factors and fluxes for the separation of ammonia and hydrocarbons over hydrogen or nitrogen, based on preferential adsorption. The results indicate promise for these high performance MFI membranes to be used for industrial  $NH_3/H_2/N_2$  or hydrocarbon/ $H_2$  separation applications.

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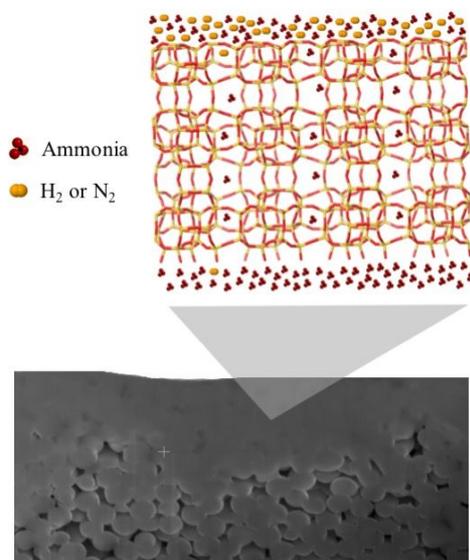
## Conflicts of interest

The authors declare no competing financial interest.

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## Table of contents



MFI membranes, made from secondary growth of layers of directly synthesized nanosheets, exhibited high separation factor and flux for the separation of ammonia over hydrogen and nitrogen based on preferential ammonia adsorption, suggesting possibilities for industrial use in processes encountered in ammonia synthesis and utilization. The membranes also exhibit a high performance for hydrogen separation from hydrocarbons.