RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

COMMUNICATION

Desorption-controlled separation of natural gas alkanes by zeolite membranes

Cite this: DOI: 10.1039/xoxxoooooox

R. Dragomirova,[a] M. Stöhr,[a] C. Hecker,[b] U. Lubenau,[c] D. Paschek,[d] S. Wohlrab*[a]

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

The performance of porous membranes is tremendously influenced by desorption as alkane separations by a pressure stable MFI membrane revealed. High membrane selectivities as well as permeation fluxes are to be traced back to the fact that a reduced permeate pressure significantly decreases the loading gradient of the adsorbed molecules in the membrane.

In regard to the continuing demand on carbon feedstocks, C_{2-5} alkanes from natural gas possess a tremendous potential.[1-6] In addition to catalytic alkane conversions the substitution of present separation technologies for natural gas alkanes by low energetic alternatives[7-9] would be the essential economic progresses for their increased use in chemical industry. In this context, membranes based on silicon rubber have currently found practical application.[7] However, with typical mixed-gas propane/methane selectivities of 3-5 and butane/methane selectivities of 5-10 they are preferably used for natural gas processing. Higher selectivities are necessary for targeted alkane isolation and were reported for more advanced polymer membranes.[10] Even so, heavy hydrocarbons cause swelling of polymer membranes, leading to increased permeation for all components and a decrease of the separation ability over time.[11] So far, non-swellable zeolite membranes were not applicable since they lost in direct competition with polymer membranes in terms of selectivity. However, due to their specific properties, such as a well-defined pore system, pressure and thermal stability as well as their non-swellability zeolite membranes should be an alternative in the application of selective membrane separation processes.[12, 13]
The understanding of the underlying interactions between zeolite membrane and adsorbed molecules is the key for a successful application. A five-step step transport model has been proposed for adsorption driven zeolite membrane separation including: 1) adsorption at the external surface; 2) transport from the external surface into the pores; 3) intracrystalline transport; 4) transport from the pores to the external surface and 5) desorption from the external surface.[14, 15] Xiao and Wei differentiate between activated gas transport and surface diffusion during intracrystalline diffusion in microporous materials.[16] According to van de Graaf the permeation flux through the zeolite membrane by surface diffusion can be expressed by Eq. (1).[17]

$$N_i^s = D_i^s \rho q_{sat,i} \nabla \ln(1-\theta_i) \; with \; D_i^s = D_i^{s,0} exp\left\{\frac{-E_a^s}{RT}\right\} \quad (1)$$

N_i^s is the flux of the component i in [mol m^{-2} s^{-1}] and D_i^s is the diffusivity of component i in [m^2 s^{-1}]; $q_{sat,i}$ and θ_i represent the saturation concentration in the zeolite in [mol g^{-1}] and the occupancy in the membrane, respectively; ρ is the material density in [g m^{-3}].
Additional to differences in occupancy/loading of components, a preferential adsorption of one component hinders the permeation of the other one leading to higher separation selectivities.[18] For example, the preferential enrichment of a higher alkane from mixtures consisting of methane/ethane or ethane/isobutene was reported for silicalite-1 and composite alumina–MFI zeolite membranes, respectively.[19, 20] Thus, the operating parameters - pressure and temperature - are considered to be the important control variables influencing the membrane performance.[15, 19] The temperature essential to achieve the maximum permeation flux of a single component through the membrane increases with the adsorption strength of the molecule.[21, 22] The positive influence of an increased pressure difference on the permeation flux through MFI membranes of n-butane single gas was already described by Gump et al.[23] With regard to the separation of alkanes, the principal applicability of MFI membranes could already have been demonstrated.[24, 25] Recently, we showed that with increasing feed pressures, a higher n-butane adsorption/condensation probability at the membrane surface could be achieved, hindering methane to permeate and thus improving the separation selectivity.[25-27] While the impact of diffusion and adsorption on zeolite membranes became clear it was still not effective enough to reach polymer membrane performances.
For this work we used pressure stable nearly defect-free MFI-membranes with a Si/Al ratio of 270 and layer thicknesses of approximately 40 µm on inert α-Al_2O_3 supports prepared by a two-step synthesis process (S1., Fig. S1, ESI†).[25] The customized MFI membranes 22 x 10^{-4} m^2 equipped with a MFI sublayer acting as mechanical stabilizer were used in single and mixed gas permeation experiments with methane and n-butane. The separation ability of the membrane is characterized by the so called separation factor - the molar ratio of n-butane over methane in the permeate divided by the

RSC Advances Accepted Manuscript

molar ratio of n-butane over methane in the retentate. From configurational biased Monte Carlo (CBMC) simulations realistic adsorption isotherms for single as well mixed gases were computed as previously reported.[27]

Calculated single gas adsorption isotherms of 100 vol% methane and 100 vol% n-butane, respectively, locate the loading of both components and the mechanism of the intracrystalline diffusion in such a membrane therewith (Fig. S2, ESI†). The low loading of methane and high loading of n-butane at the feed and the permeate side of a MFI membrane under operating conditions are illustrated in Fig 1a. At increasing temperatures - from 293 to 348 K - a more pronounced decline in the loading of methane at the feed side is obvious, whereas temperature variation changes feed loading of n-butane less. At lower permeate pressure and increased temperature the loading of n-butane at the permeate side is significantly decreased, while nearly no methane molecule is adsorbed below 0.05 bar. The significance of the loading on the permeation flux can be conjectured from a series of single gas permeation measurements accomplished at different temperatures with both, methane and n-butane (Fig. 1b and 1c – circles), and the obviously underlying surface diffusion model (1) for both components (Fig. 1b and 1c – lines; S2., ESI†).

In the case of methane (Fig 1b), the loading slope and therewith the flux decreases with increasing temperature, whereas for the case of n-butane (Fig 1c) the flux increases. From Fig. 1b it can be seen that reducing the permeate pressure results in an almost linear increase of the permeation flux for methane. Obviously, the process is quite temperature dependent, where an increase in the temperature leads to reduction in the permeation flux. At a permeate pressure of 0.01 bar the permeation fluxes are 2437 L $h^{-1}m^{-2}$ and 1850 L $h^{-1}m^{-2}$ at 298 and 348 K, respectively. Similar temperature dependence of the permeation fluxes of methane as a function of feed pressure was reported by Burggraaf at al.[22] The observed flattening of the experimental permeation flux of methane (Fig. 1b, circles) at low permeate pressures is due to the feed streams used. At permeate pressures of approximately 0.2 bar nearly the whole feed stream of methane permeates through the membrane. An increase of the feed flux from 6 L/h to 12 L/h results in a nearly linear increase in permeation (Fig. S3, ESI†). In case of n-butane, due to the stronger molecular interactions with the MFI structure smaller overall permeation fluxes were detected (Fig. 1c, circles). However, the reduced pressure on the permeate side improves apparently the permeation as a consequence of the enhanced surface diffusion caused by the decreased loading of n-butane molecules at the permeate side. Increase in the concentration gradient of n-butane at lower permeate pressures due to the decreased coverages on the permeate side was described as well by Gump et al.[23] In contrast to sweep gas usage vacuum reduces the diffusion resistance of the permeating species. Furthermore, a higher mobility of the adsorbed molecules is favoured by the moderate temperature increase and contributes to a higher flux. Additionally, as further experiments (Fig. S4, ESI†) show, increase in the feed pressure to 2 bar gives rise to higher permeation fluxes for n-butane which is still exponentially depended on the reduced permeate pressure, whereas the whole feed of methane permeates through the membrane at permeate pressure below 0.8 bar due to the higher pressure difference and its smaller molecule size.

The different permeation characteristics of both alkanes, methane and n-butane, at reduced permeate pressures have a significant influence on the separation of both molecules. The calculated mixed gas-adsorption isotherms for a model mixture consisting of 92 vol% methane and 8 vol% n-butane reveals the preferable adsorption of n-butane in the operating regime (see Fig. S5, ESI†). Schematic representation of the loading at the feed and permeate side is depicted in Fig 2a. Here, the loading slope of n-butane in mixture is more pronounced in comparison to the loading of the respective single gas adsorption isotherm. Moreover, an increase in processing temperature leads to even higher change in loading of n-butane. For methane a practically negligible small loading in the operating pressure range is obvious.

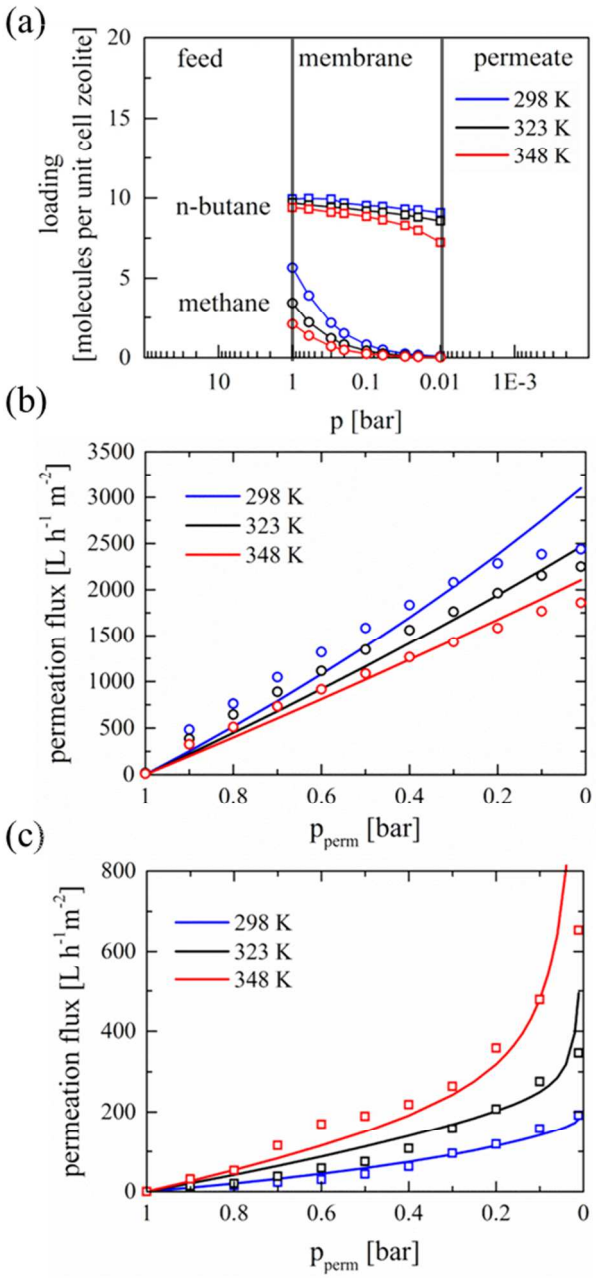

Fig. 1: Single gas permeation of methane and n-butane in MFI-membranes, a) Schematic representation of the loading of pure methane and pure n-butane at the feed and permeate side, and as guide for the eyes the loading across the membrane calculated from the adsorption isotherms. b) Experimental permeation fluxes of methane (circles) and predictions of the permeation flux according to the surface diffusion model (lines) at stepwise reduced permeate pressure at feed pressure of 1 bar. c) see b) but for n-butane.

Arruebo et al. had given an indirect evidence on the significance of desorption of the permeating species[24] but experiments failed since pressure stable membranes were not available. Since we use pressure stable membranes[25] we clearly can demonstrate the tremendous

RSC Advances Accepted Manuscript

This journal is © The Royal Society of Chemistry 2012

influence of desorption on the separation performance. Experiments with the model mixture were conducted at 298 K, 323 K and 348 K, respectively. In this case the feed pressure was adjusted to 2 bar and a feed flow of 6 L/h was applied. Additionally, separation experiments with feed pressure of 1 bar were conducted (Fig. S6, ESI†). In Fig. 2b and 2c the permeation fluxes and the development of the separation factors are displayed. By reducing the permeate pressure and thus decreasing the loading of the preferably adsorbed n-butane molecules an exponentially improved separation is observed.

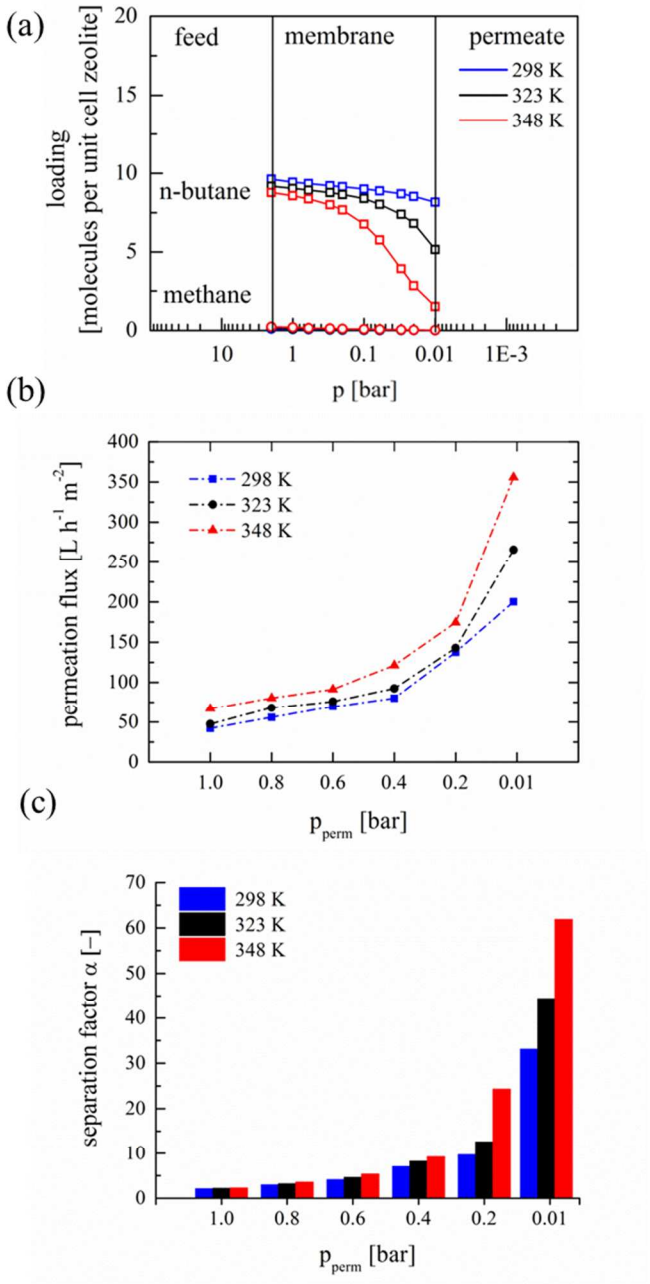

Fig. 2: Mixed gas permeation experiments of mixture comprising 92 vol% methane and 8 vol% n-butane, a) schematic representation of the loading on the feed and permeate side, and as guide for the eyes the loading across the membrane calculated from the adsorption isotherms; b) permeation fluxes and c) separation factor $\alpha_{C4/C1}$ at constant feed pressure of 2 bar at stepwise reduced permeate pressure.

The enhanced selectivity could be attributed to the relatively higher permeation flux of n-butane as a direct result of the increased mobility due to higher loading gradient between feed and reduced permeate pressure. Moreover, a comparable exponential dependence of the permeation flux at the permeate side as the one observed in the single gas measurements for n-butane was found. Furthermore, moderate increase of the temperature intensifies the process and leads to even higher permeation fluxes above 350 L h^{-1} m^{-2} and excellent separation factors above 60 which are in the range of advanced polymer membranes[10]. It is obvious that the increase in desorption is directly correlated with the enhanced permeation flux. The increased permeation flux itself is the influencing parameter for the selectivity since more preferably adsorbed n-butane permeates across the membrane at lower permeate-pressures.

In conclusion, the impact of desorption on the separation performance of MFI-membranes is evidenced. The enhanced separation is governed to a great extent by the improved desorption of the mainly adsorbed species, representing a key aspect in the adsorptive separation of natural gas alkanes. Thus, under permeate vacuum inorganic zeolite membranes could be an alternative to polymer membranes for the separation of natural gas alkanes.

Financial support by DFG SPP1570 and AiF "Otto von Guericke" e.V. is acknowledged.

Notes and references

[a] Leibniz Institute for Catalysis at the University Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany. E-mail: sebastian.wohlrab@catalysis.de

[b] Technical University Freiberg, Institute for Electronic and Sensor Materials, Gustav-Zeuner-Str. 3, D-09599 Freiberg, Germany

[c] DBI Gas-und Umwelttechnik GmbH, Theklaer Str. 42, D-04347 Leipzig, Germany

[c] Institute für Chemie, Abteilung Physikalische Chemie, University of Rostock, Dr.-Lorenz-Weg 1, D-18059 Rostock, Germany

† Electronic Supplementary Information (ESI) available: membrane preparation and characterization by permporometry; calculated single gas adsorption isotherms, permeation flux calculation and determination; mixed gas adsorption isotherms and separation experiments. See DOI: 10.1039/c000000x/

1. M. Baerns and O. Buyevskaya, *Catal. Today*, 1998, **45**, 13-22.
2. M. Sun, J. Zhang, P. Putaj, V. Caps, F. Lefebvre, J. Pelletier and J.-M. Basset, *Chemical Reviews*, 2013, **114**, 981-1019.
3. F. Cavani, N. Ballarini and A. Cericola, *Catal. Today*, 2007, **127**, 113-131.
4. T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chemical Reviews*, 2005, **105**, 2329-2364.
5. J. L. Nieto, *Top. Catal.*, 2006, **41**, 3-15.
6. J. Brazdil, *Top. Catal.*, 2006, **38**, 289-294.
7. R. W. Baker and K. Lokhandwala, *Ind. Eng. Chem. Res.*, 2008, **47**, 2109-2121.
8. C. A. Scholes, G. W. Stevens and S. E. Kentish, *Fuel*, 2012, **96**, 15-28.
9. P. Bernardo, E. Drioli and G. Golemme, *Ind. Eng. Chem. Res.*, 2009, **48**, 4638-4663.
10. Y. Yampolskii, L. Starannikova, N. Belov, M. Bermeshev, M. Gringolts and E. Finkelshtein, *J. Membr. Sci.*, 2014, **453**, 532-545.

RSC Advances Accepted Manuscript

11. K. Ohlrogge and T. Brinkmann, *Ann. N. Y. Acad. Sci.*, 2003, **984**, 306-317.
12. J. Caro and M. Noack, *Microporous Mesoporous Mater.*, 2008, **115**, 215-233.
13. A. Tavolaro and E. Drioli, *Advanced Materials*, 1999, **11**, 975-996.
14. R. M. Barrer, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1123-1130.
15. W. J. W. Bakker, F. Kapteijn, J. Poppe and J. A. Moulijn, *J. Membr. Sci.*, 1996, **117**, 57-78.
16. J. Xiao and J. Wei, *Chem. Eng. Sci.*, 1992, **47**, 1123-1141.
17. J. M. van de Graaf, F. Kapteijn and J. A. Moulijn, *J. Membr. Sci.*, 1998, **144**, 87-104.
18. J. Coronas and J. Santamaría, *Separation & Purification Reviews*, 1999, **28**, 127-177.
19. J. M. van de Graaf, E. van der Bijl, A. Stol, F. Kapteijn and J. A. Moulijn, *Ind. Eng. Chem. Res.*, 1998, **37**, 4071-4083.
20. M. Jiang, M. Eic, S. Miachon, J.-A. Dalmon and M. Kocirik, *Sep. Purif. Technol.*, 2001, **25**, 287-295.
21. W. J. W. Bakker, L. J. P. Van Den Broeke, F. Kapteijn and J. A. Moulijn, *AIChE J.*, 1997, **43**, 2203-2214.
22. A. J. Burggraaf, Z. A. E. P. Vroon, K. Keizer and H. Verweij, *J. Membr. Sci.*, 1998, **144**, 77-86.
23. C. J. Gump, X. Lin, J. L. Falconer and R. D. Noble, *J. Membr. Sci.*, 2000, **173**, 35-52.
24. M. Arruebo, J. Coronas, M. Menéndez and J. Santamaría, *Sep. Purif. Technol.*, 2001, **25**, 275-286.
25. S. Wohlrab, T. Meyer, M. Stöhr, C. Hecker, U. Lubenau and A. Oßmann, *J. Membr. Sci.*, 2011, **369**, 96-104.
26. K. Neubauer, U. Lubenau, C. Hecker, B. Lücke, D. Paschek and S. Wohlrab, *Chem. Ing. Tech.*, 2013, **85**, 713-722.
27. K. Neubauer, R. Dragomirova, M. Stöhr, R. Mothes, U. Lubenau, D. Paschek and S. Wohlrab, *J. Membr. Sci.*, 2014, **453**, 100-107.

RSC Advances Accepted Manuscript

 This journal is © The Royal Society of Chemistry 2012