CHEMISTRY OF MATERIALS
Communication

Chem. Mater. **2010,** *22,* 4353–4355 4353
DOI:10.1021/cm1016189

Cationic Polymer Used to Capture Zeolite Precursor Particles for the Facile Synthesis of Oriented Zeolite LTA Molecular Sieve Membrane

Aisheng Huang* and Jürgen Caro

Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Callinstrasse 3A, D-30167 Hannover, Germany

Received June 10, 2010
Revised Manuscript Received July 13, 2010

Zeolites are widely used as catalysts, ion exchangers, and adsorbents because of their uniform pore structure and high thermal stability. Apart from the use of zeolites as powders, supported zeolite layers are of interest for many potential applications. In the last 25 years, many research efforts have been focused on the preparation of supported zeolite layers as separators, reactors, sensors, and electrical insulators.[1−6] To date, for example, MFI,[7,8] DDR,[9] LTA,[10−12] FAU,[13,14] CHA,[15,16] and AFI[17,18] type membranes have been successfully prepared for gas separation. Among these molecular sieve membranes, only the LTA (NaA) zeolite membranes are produced at an industrial scale for the dewatering of bioethanol due to its strongly hydrophilicity in combination with small pore size of about 0.4 nm.[19] Indeed, LTA zeolite membranes show excellent performance with extremely high separation factors in hydrophilic separation.[20−22] There are, however, only a few reports about separation of gas mixtures on LTA zeolite membranes, and all the separation factors reported are lower than the Knudsen coefficient with the exception of the separation of O_2/N_2[23] and our recent report of LTA membrane prepared on 3-aminopropyltriethoxysilane (APTES) modified supports.[10] Aoki et al.[11] prepared LTA zeolite membrane by secondary growth method using seeding. Gas permeation measurements indicated that the mixture separation factors were lower than the Knudsen coefficient although the ideal separation factors were higher than those. Xu et al. reported microwave synthesis of high-permeances LTA zeolite membrane with H_2/n-C_4H_8 ideal separation factors of 9.8.[24] It is often found that LTA zeolite membranes contain intercrystalline defects, which are sufficiently large to prevent selective separation of gases by size-exclusion, although these membranes show high liquid-phase selectivity in the separation of water from water/organic mixtures.[25,26]

It was well-recognized that control of the microstructure of the zeolite membranes, such as grain orientation and grain boundary, plays an important role for their performances.[27,28] Therefore, intense research efforts have been made toward the preparation of oriented zeolite membranes,[29] mainly focused on the preparation of *b*-oriented MFI membranes because *b*-oriented MFI membranes show superior separation performance.[30−32] Recently, Lai et al.[33] reported the synthesis of *b*-oriented ZSM-5 membrane with a high p-xylene/o-xylene selectivity of about 500.

There are only a few reports of oriented LTA zeolite membrane/film. Hedlund et al., for the first time,

*To whom correspondence should be addressed. E-mail: aisheng.huang@pci.uni-hannover.de.

(1) Caro, J.; Noack, M. *Microporous Mesoporous Mater.* **2008**, *115*, 215.
(2) Tavolaro, A.; Drioli, E. *Adv. Mater.* **1999**, *11*, 975.
(3) McLeary, E. E.; Jansen, J. C.; Kapteijn, F. *Microporous Mesoporous Mater.* **2006**, *90*, 198.
(4) Casanave, D.; Giroir-Fendler, A.; Sanchez, J.; Loutaty, R.; Dalmon, J. *Catal. Today* **1995**, *25*, 309.
(5) Yu, M.; Falconer, J. L.; Amundsen, T. J.; Hong, M.; Noble, R. D. *Adv. Mater.* **2007**, *19*, 3032.
(6) Wang, Z.; Wang, H.; Mitra, A.; Huang, L.; Yan, Y. *Adv. Mater.* **2001**, *13*, 746.
(7) Yan, Y. S.; Davis, M. E.; Gavalas, G. R. *Ind. Eng. Chem. Res.* **1995**, *34*, 1652.
(8) van de Graaf, J. M.; van der Bijl, E.; Stol, A.; Kapteijn, F.; Moulijn, J. A. *Ind. Eng. Chem. Res.* **1998**, *37*, 4071.
(9) Kanezashi, M.; O'Brien-Abraham, J.; Lin, Y. S.; Suzuki, K. *AIChE J.* **2008**, *54*, 1478.
(10) Huang, A.; Liang, F.; Steinbach, F.; Caro, J. *J. Membr. Sci.* **2010**, *350*, 5.
(11) Aoki, K.; Kusakabe, K.; Morooka, S. *J. Membr. Sci.* **1998**, *141*, 197.
(12) Huang, A.; Liang, F.; Steinbach, F.; Gesing, T. M.; Caro, J. *J. Am. Chem. Soc.* **2010**, *132*, 2140.
(13) Kusakabe, K.; Kuroda, T.; Murata, A.; Morooka, S. *Ind. Eng. Chem. Res.* **1997**, *36*, 649.
(14) Nikolakis, V.; Xomeritakis, G.; Abibi, A.; Dickson, M.; Tsapatsis, M.; Vlachos, D. G. *J. Membr. Sci.* **2001**, *184*, 209.
(15) Hong, M.; Li, S.; Falconer, J. L.; Noble, R. D. *J. Membr. Sci.* **2008**, *307*, 277.
(16) Carreon, M.; Li, S.; Falconer, J. L.; Noble, R. D. *J. Am. Chem. Soc.* **2008**, *130*, 5412.
(17) Mintova, S.; Mo, S.; Bein, T. *Chem. Mater.* **1998**, *10*, 4030.
(18) Girnus, I.; Pohl, M.; Richter-Mendau, J.; Schneider, M.; Noack, M.; Venzke, D.; Caro, J. *Adv. Mater.* **1995**, *7*, 711.
(19) Morigami, Y.; Kondoa, M.; Abe, J.; Kita, H.; Okamoto, K. *Sep. Purif. Technol.* **2001**, *25*, 251.
(20) Kondo, M.; Komori, M.; Kita, H.; Okamota, K. *J. Membr. Sci.* **1997**, *133*, 133.
(21) Shah, D.; Kissick, K.; Ghorpade, A.; Hannah, R.; Bhattacharyya, D. *J. Membr. Sci.* **2000**, *179*, 185.
(22) Zhu, W.; Gora, L.; van den Berg, A. W. C.; Kapteijn, F.; Jansen, J. C.; Moulijn, J. A. *J. Membr. Sci.* **2005**, *253*, 7.
(23) Yin, X.; Zhu, G.; Yang, W.; Li, Y.; Zhu, G.; Xu, R.; Sun, J.; Qiu, S.; Xu, R. *Adv. Mater.* **2005**, *17*, 2006.
(24) Xu, X.; Yang, W.; Liu, J.; Lin, L. *Adv. Mater.* **2000**, *12*, 195.
(25) Noack, M.; Kölsch, P.; Dittmar, A.; Stöhr, M.; Georgi, G.; Schneider, M.; Dingerdissen, U.; Feldhoff, A.; Caro, J. *Microporous Mesoporous Mater.* **2007**, *102*, 1.
(26) Caro, J.; Albrecht, D.; Noack, M. *Sep. Purif. Technol.* **2009**, *66*, 143.
(27) Bonilla, G.; Vlachos, D. G.; Tsapatsis, M. *Microporous Mesoporous Mater.* **2001**, *42*, 191.
(28) Caro, J.; Noack, M.; Kolsch, P.; Schafer, R. *Microporous Mesoporous Mater.* **2000**, *38*, 3.
(29) Lee, J.; Lee, Y.; Tae, E.; Park, Y.; Yoon, K. *Science* **2003**, *301*, 818.
(30) Lovallo, M. C.; Tsapatsis, M. *AIChE J.* **1996**, *42*, 3020.
(31) Liu, Y.; Li, Y.; Yang, W. *J. Am. Chem. So.* **2010**, *132*, 1768.
(32) Aguado, S.; McLeary, E. E.; Nijmeijer, A.; Luiten, M.; Jansen, J. C.; Kapteijn, F. *Microporous Mesoporous Mater.* **2009**, *120*, 165.
(33) Lai, Z.; Bonilla, G.; Diaz, I.; Nery, J.; Sujaoti, K.; Amat, M. A.; Kokkoli, E.; Terasaki, O.; Thompson, R. W.; Tsapatsis, M.; Vlachos, D. G. *Science* **2003**, *300*, 456.

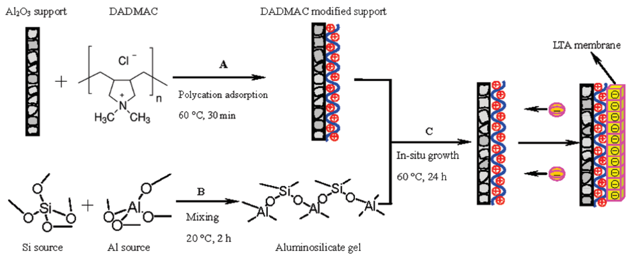

Figure 1. Schematic diagram for preparation of LTA zeolite membrane by using the cationic polymer DADMAC to capture zeolite precursor particles during hydrothermal synthesis.

prepared an ultrathin oriented LTA zeolite film on the single-crystal alumina (0001) wafer, which showed a parallel orientation of the (h00) face relative to the support plane as judged by X-ray diffraction (XRD).[34] Thereafter, Tsapatsis's group reported preferentially (h00) oriented LTA zeolite films on silicon wafers and glass slides by controlling the pH to get an electrostatic attraction between support and seeds.[35] Yoon et al. have developed a novel "two-component modification" strategy for assembly of a highly (h00) oriented LTA zeolite film on glass slides via covalent linkages.[36] However, in these preceding studies on oriented zeolite films, no separation performances for gas mixtures were reported.

Cationic polymers have been previously used for seeding a support before hydrothermal synthesis. By van der Waals adsorption of positively charged polymers like poly-(diallyldimethylammonium chloride) (poly-DADMAC), negatively charged zeolite nanoparticles can be deposited on the support surface and used as seeds for further secondary growth.[34] Different from the previous study, in the present work, the cationic polymers adsorbed on the support surface are used to capture LTA zeolite particles from the batch during in situ hydrothermal synthesis. It is expected that because of the electrostatic interaction, the negatively charged LTA zeolite particles can homogenously and easily migrate to the positively charged support surface, facilitating the formation of a uniform and dense zeolite LTA membrane, as shown in Figure 1.

Figure 2a−c shows the SEM top view of the LTA zeolite membrane at different magnifications on the DADMAC-modified α-Al_2O_3 support. The SEM images indicate that the support surface is completely covered by well intergrown uniform and oriented cone-shaped LTA crystals, and no cracks, pinholes, or other defects can be observed. From the cross-section shown in Figure 2d, it can be seen that the well intergrown membrane has a thickness of about 4.0 μm. To minimize the surface energy of the DADMAC-modified support, the zeolite crystals prefer to pack as close as possible,[37] and finally self-assemble to a highly ordered and dense film. On the contrary, no dense LTA zeolite membrane could be formed on the nonmodified Al_2O_3 support, and the zeolite layer was less intergrown with rough surface.[10] Figure S1 in the Supporting Information shows the Zeta potential of Al_2O_3, DADMAC-modified Al_2O_3, and LTA zeolite particles suspended in water as function of pH. It can be seen that a positive surface charge can be generated in a wide pH range when the Al_2O_3 support was treated with DADMAC, and consequently, the negatively charged zeolite LTA nutrients can be attracted. We can expect, therefore, that a positive surface charge of the support at the pH ∼11 of the membrane formation is helpful to electrostatically attract the negatively charged LTA nutrients thus promoting the nucleation and growth of the LTA membrane. Actually, a rather dense LTA layer with nanoparticles have been formed on the DADMAC-modified Al_2O_3 support in a rather short synthesis time (see Figure S2 in the Supporting Information).

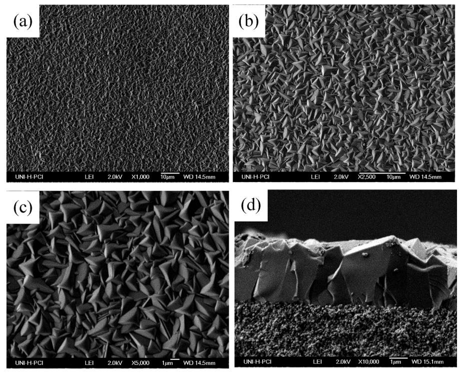

Figure 2. Typical SEM images of the LTA zeolite membrane prepared on the DADMAC-modified Al_2O_3 support, showing (a−c) top view with different magnification and (d) cross-section.

The formation of oriented LTA zeolite membrane was confirmed by XRD as shown in Figure 3. Different from the randomly oriented XRD pattern of LTA zeolite membrane prepared on the nonmodified support (Figure 3c) and LTA zeolite powder (Figure 3d), the LTA membrane prepared on the DADMAC-modified support shows a stronger (222) peak (Figure 3b), whereas the intensity of the (h00) peaks is drastically reduced, indicating that the (222) faces of the LTA crystals are oriented perpendicular to the substrate surface. A similar (222) oriented LTA zeolite film was prepared on 3-aminopropyltrimethoxysilane modified stainless steel.[38] In general, the nano/microcrystals tend to maximize their contact with the support when they adhere onto the support surface.[39] Probably, the zeolite crystals are liable to attach to the DADMAC-modified alumina surface with their C3 axis ([222] direction) perpendicular to the support surface in order to maximize the cation−anion contact.[40] Applying the identical synthesis procedure, similar (222) oriented LTA membrane is prepared on a DADMAC-modified flat glass (see Figure S3 in the Supporting Information). More research is needed to clarify the

(34) Hedlund, J.; Schoeman, B.; Sterte, J. *Chem. Commun.* **1997**, 1193.
(35) Boudreau, L.; Kuck, J.; Tsapatsis, M. *J. Membr. Sci.* **1999**, *152*, 41.
(36) Kulak, A.; Lee, Y. J.; Park, Y. S.; Yoon, K. B. *Angew. Chem., Int. Ed.* **2000**, *39*, 950.
(37) Kulak, A.; Lee, Y. J.; Park, Y. S.; Kim, H. S.; Lee, G. S.; Yoon, K. B. *Adv. Mater.* **2002**, *14*, 526.
(38) Yang, G.; Zhang, X.; Liu, S.; Yeung, K. L.; Wang, J. *J. Phys. Chem. Solids* **2007**, *68*, 26.
(39) Yoon, K. B. *Acc. Chem. Res.* **2007**, *40*, 29.
(40) Park, J. S.; Jeong, N. C.; Lee, Y. J.; Kim, M. J.; Yoon, K. B. *J. Nanosci. Nanotechnol.* **2010**, *10*, 370.

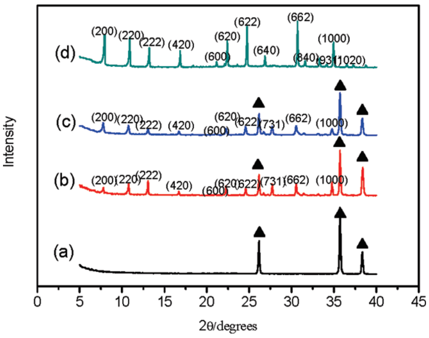

Figure 3. XRD patterns of the (a) Al_2O_3 support, (b) LTA zeolite membrane M3 prepared on DADMAC-modified Al_2O_3 support, (c) LTA zeolite membrane M1 prepared on nonmodified Al_2O_3 support, and (d) LTA zeolite powder: (▲), Al_2O_3 support; (not marked), LTA zeolite.

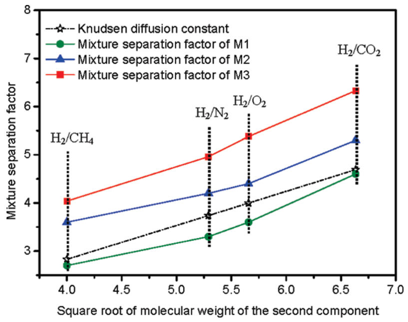

Figure 4. Mixture separation factors of H_2 from equimolar mixtures with the gases CH_4, N_2, O_2 and CO_2 on LTA (NaA) membrane. The dashed line indicates the separation factors if a Knudsen separation mechanism would take place. M1, prepared on nonmodified Al_2O_3 support; M2, prepared on APTES modified Al_2O_3 support [10]; M3, prepared on DADMAC-modified Al_2O_3 support.

preferred (222) orientation mechanism on the DADMAC-modified support. Further, it can be seen that all peaks besides the signals from the Al_2O_3 support match well with those of the zeolite LTA structure, indicating that pure LTA zeolite membranes is formed on the DADMAC-modified support.

The LTA (NaA) membrane was evaluated in mixture gas separation. The volumetric flow rates of the 1:1 binary mixtures of H_2 with CH_4, N_2, O_2 and CO_2 were measured using the Wicke-Kallenbach technique (see Figure S4 in the Supporting Information). Figure 4 shows the mixture separation factors of hydrogen from other gases on the LTA membrane versus the square root of molecular weight of the second component. The LTA membrane prepared on the nonmodified support (M1 in Figure 4) exhibits a poor gas separation performance, and all mixture separation factors are lower than the corresponding Knudsen coefficients.[10] As shown in Figure 4, both the LTA membranes on the APTES and poly-DADMAC-modified supports (M2 and M3 in Figure 4) display a better separation performance. The LTA membrane grown on the DADMAC-modified Al_2O_3 supports with oriented LTA crystals in the membrane layer shows mixture separation factors of H_2/CH_4, H_2/N_2, H_2/O_2 and H_2/CO_2 with 4.0, 5.0, 5.4, and 6.3, respectively, which are higher than the corresponding Knudsen coefficients of 2.8, 3.7, 4.0, and 4.7. Besides the relative high mixture separation factors, it should be noted that the H_2 permeance of the oriented LTA zeolite membrane is higher than that of our previous report (see Figure S5 in the Supporting Information). It is well-known that the control of the preferential orientation of the membrane has a great effect on the membrane performances.[33] It is possible that the oriented growth can minimize the defect density and the transport pathways through the grain boundaries, thus leading to enhancement of the separation performances. The H_2 permeance increases from 4.6×10^{-7} to 5.0×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, whereas the mixture separation factor of H_2/CH_4 is slightly reduced from 4.0 to 3.7 when the temperature increases from 298 to 373 K (see Figure S5 in the Supporting Information). It is found that DADMAC treatment is helpful to enhance the membrane reproducibility (see Table S1 in the Supporting Information). The average H_2/CH_4 selectivity is 3.94 ± 0.18 (standard deviation) for the four membranes in Table S1 in the Supporting Information.

As expected, the permeances of n- and i-butane through the Na-LTA membrane are negligible since both kinetic diameter of n-butane (0.43 nm) and i-butane (0.51 nm) are larger than the pore size of Na-LTA. After ion exchange of the Na^+ by Ca^{2+}, the single-component permeances of n- and i-butane through the Ca-LTA membrane at 25 °C are found to be 1.27×10^{-7} and 8.32×10^{-9} mol m^{-2} s^{-1} Pa^{-1}, respectively. An ideal separation factor (ratio of the single component fluxes) of 15.3 can be derived which is again a clear indication of molecular sieving.

In conclusion, we have prepared a (222) oriented LTA zeolite membrane with improved gas separation performance by using the cationic polymer DADMAC to capture zeolite nutrients during the hydrothermal synthesis. The DADMAC-modified alumina supports keep their positive surface charge (Zeta potential) in the alkaline region thus attracting the negatively charged building blocks of the zeolite formation, leading to the formation of uniform and dense LTA zeolite membrane. The oriented LTA zeolite membrane prepared on DADMAC-modified alumina supports display a better separation performance than a randomly oriented LTA zeolite membrane.

Acknowledgment. Financial support by DFG, as a part of the European joint research project "International Research Group: Diffusion in Zeolites" of DFG, CNRS a,nd EPSRC (Ca147/11-3), is acknowledged. Dr. A. Feldhoff is thanked for support in electron microscopy. P. Wagner is thanked for help in measurement of Zeta potential.

Supporting Information Available: Experimental details; (Figure S1) Zeta potential of Al_2O_3, DADMAC-modified Al_2O_3, and LTA zeolite particles; (Figure S2) SEM image of the LTA membrane on DADMAC-modified Al_2O_3 support; (Figure S3) SEM image and XRD of the LTA zeolite membrane on DADMAC-modified glass; (Figure S4) measurement equipment of gas permeation; (Figure S5) H_2/CH_4 selectivity and permeance of the LTA zeolite membrane; (Table S1) H_2/CH_4 separation properties for LTA membranes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/