

제올라이트 분리막: 조성 변경을 통한 분리막 성질의 조절

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Zeolite Membranes: Functionalizing of Properties by Tailored Compositions

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요약: 분리막을 이용한 분리 기술은 에너지 소요가 적다. 제올라이트를 기반으로 제작한 분리막의 경우, 결정 구조 내에 작은 분자 크기의 기공을 갖고 있어 이를 이용하여 가혹한 조건에서도 분리가 가능하기 때문에, 그 관심도가 높다. NaA (LTA 유형의 제올라이트) 제올라이트의 경우, 산업적으로 유기 용매에서 수분을 제거하는 데 많이 사용되는 데, 해당 기공 크기나 열적/수열안정성은 제올라이트 내부나 외부의 원소를 바꿔줌으로써 조절할 수 있다. 더 작은 0.28 nm 크기를 지닌 SOD 유형의 제올라이트의 경우, 수소나 물 분리에 적합하여 그 관심도가 높아지고 있으며, 이 제올라이트 유형 또한, 이온 교환과 같은 방법으로 성질을 변경할 수 있다. 제올라이트는 주변 기술 및 공정 조건에 맞게 작은 분자들을 적절하게 분리할 수 있는 분리막을 창출할 수 있다는 장점을 지닌 소재이다.

Abstract: Membrane separation is a technology of low energy consumption. Membranes made of zeolites are of great interest because their fixed and open pores in the size of small molecules inside crystalline structures allow separation processes under harsh conditions. While zeolite NaA (LTA-type) is industrially used for dewatering of organic solvents, its pore size and thermal and hydrothermal stability can be tuned by exchange of framework and extra-framework elements. SOD with pores of only 0.28 nm is of great interest for H₂- und H₂O-separation and also can be tuned by ion exchange. Zeolites open the opportunity to create membranes of adapted separation behavior for small molecules in conditions of surrounding technical processes.

Keywords: zeolites, microporous membranes, molecular sieve, gas separation from mixtures

1. Introduction

Sustainable social development requires novel technologies with less environmental impact. Energy consumption effects environment dramatically. Development of processes of reduced energy consumption is therefore one of the big topics of science and engineering.

Separation processes are one of the basic operations in many industries. Also several techniques are practically used thermal driven processes are responsible for 80% of the whole energy consumption of all industrial separation processes. Distillation followed by drying and evaporation are the most energy consuming separation processes. By using membrane technologies energy consumption can be reduced in comparison to dis-

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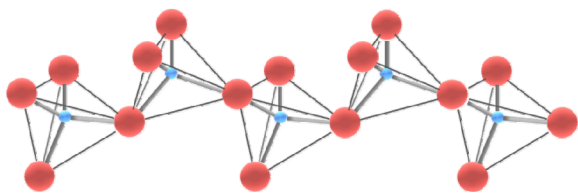


Fig. 1. Chain of tetrahedrally configured silicon and oxygen.

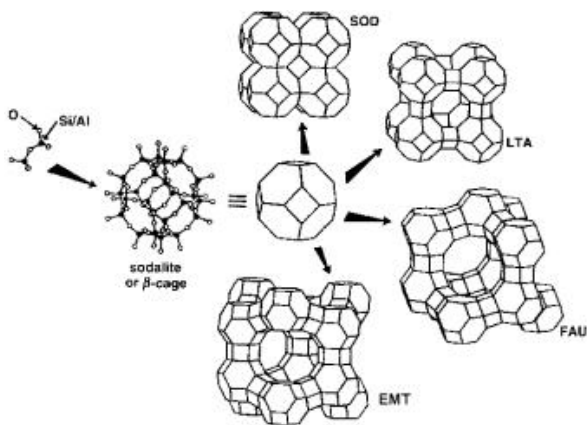


Fig. 2. Tetrahedrally configured silicon and oxygen (left) forming sodalite or the so-called β -cage. Depending on the number of units and their combination, a number of zeolite structures can thus be formed: SOD : sodalite; LTA : zeolite type A; FAU : faujasite; EMT : a hexagonal variant of FAU present in zeolite EMT-2[6].

tillation up to 85%[1].

Membranes made of polymers are dominating the membrane market. Wastewater cleaning and seawater desalination are examples of very large membrane application. Cleaning of natural gas are first bigger application in gas separation. However, intrinsic properties of the polymers, like low thermal, chemical and mechanical stability limiting the conditions of membrane using.

Membranes made of ceramics allow membrane separation processes also in harsh conditions, like high temperatures, high pressure or in aggressive chemicals. Several materials like amorphous oxides, palladium or carbon are used or in development for nanofiltration, pervaporation and gas separation[2-5].

Zeolites are of great interest because of the crystalline structure with fixed pores in the size of small molecules. Chemical composition and crystal structure

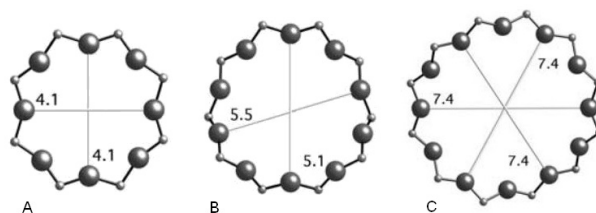


Fig. 3. Window openings composed of (A) 8 $[\text{SiO}_4]^{4-}$ -tetrahedra in LTA, (B) 10 $[\text{SiO}_4]^{4-}$ -tetrahedra in MFI and (C) 12 $[\text{SiO}_4]^{4-}$ -tetrahedra in FAU. Diameters are given in Å[7].

are the powerful tools to adjust thermal and hydrothermal stability as well as separation behavior.

2. Structural Features of Zeolites

Zeolites are crystalline tectosilicates and their chemical composition may be given with the general formula $(\text{M}^{2+}\text{M}^+)\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n \text{SiO}_2 \cdot m \text{H}_2\text{O}$. Silicon is tetrahedrally coordinated with oxygens. The $[\text{SiO}_4]^{4-}$ -tetrahedra are connected by vertex-shared oxygens (Fig. 1) thus creating a three-dimensional fully cross-linked solid framework. In Fig. 2 the β -cage as repeating element of the sodalite 3D framework is shown as an example.

Inside the crystalline structure open cages and channels are formed with entrances called *windows*. Examples of windows with different diameters are shown in Fig. 3. The size of the windows differs for the numerous zeolites and is determined by the number of $[\text{SiO}_4]^{4-}$ -tetrahedra. Depending on the crystal structure windows in the range of 0.3 and 0.9 nm can be created, which fit the size of small gas molecules. This structural particularity makes zeolites attractive for numerous of industrial applications, among them gas separation by adsorption and membrane separation.

Up to 50% aluminum can be incorporated into the framework instead of silicon (e.g. zeolite LTA). The missing positive charge of the trivalent aluminum is compensated by additional alkali or alkaline earth metal ions. These extra-framework cations can be easily exchanged which is practically used in washing agents for water softening. The extra-framework cations influ-

ence the open space in the cages and the size of the windows as well. Polar sites in zeolites with high alumina content make the crystals hydrophilic and are the reason for pore filling with water at ambient conditions. The water can be completely desorbed by heating (at temperature of 200°C or higher, depending on the zeolite type) without losing the crystalline structure of the zeolites. In low Al-containing zeolites with neutral frameworks, the cavities can be completely empty. The crystal structure of some zeolites is stable even at temperatures up to 800°C[8], an attractive feature for certain applications, e.g. catalytic cracking, at elevated temperatures.

3. Principles of Transport through Zeolites

Zeolites are characterized by pores with the size of small gas molecules. Once a gas flow through the pores starts, a strong interaction between the gas molecules and the pore walls of the zeolite lattice occurs, which can be described by the process known as configurational diffusion. Depending on the temperature and the gas molecule involved, the process is distinguished between *solid vibration model (SV)* and *gas translation model (GT)*[9].

At low temperatures and strong gas molecule-zeolite interaction, the permeating molecules are losing their gaseous character: they vibrate with the zeolite lattice and jump from one to the next adsorption site when enough energy is available. In this case the mass transfer, J_{surf} , in this case can be described by the surface diffusion model[10](Eq. 1) :

$$J_{surf} = -D_{surf} \nabla q \quad (1)$$

The driving force in this process is the gradient of surface loading across the pore length or the thickness of the membrane, ∇q .

The surface diffusion coefficient, D_{surf} , is dominated by the jump frequency $v_{surf,0}$ and jump distance λ of the molecule, as well as the activation energy E_{act} and the temperature T , according to Eq. 2 :

$$D_{surf} = \frac{1}{4} \cdot v_{surf,0} \cdot \lambda^2_{surf} \cdot \exp\left(-\frac{E_{act}}{RT}\right) = D_0 \cdot \exp\left(-\frac{E_{act}}{RT}\right) \quad (2)$$

The activation energy correlates linearly with the differential heat of adsorption ΔH . When ΔH of an adsorbed component q is known, then the surface diffusion coefficient can be calculated using Eq. 3 :

$$D_{surf}(q) = D_{surf,0} \cdot \exp\left(-\frac{\alpha \Delta H_{ad}(q)}{RT}\right) \quad (3)$$

At higher temperatures and weak molecule-zeolite interactions the molecules inside the pores retain their gaseous character and consecutively the mass transfer can be described by the gas translation (GT) model. The GT diffusion coefficient D_{GT} defined with Eq. 4 is characterized by the mean free path, λ , of the molecule, the reliability factor y , molar weight M , temperature T and activation energy $E_{A,GT}$ [11] :

$$D_{GT} = \frac{\lambda}{y} \cdot \sqrt{\frac{8RT}{\pi M}} \cdot \exp\left[-\frac{E_{act,GT}}{RT}\right] \quad (4)$$

The overall mass transfer through a zeolite material, J_{tot} , is the sum of the mass transfer caused by the gas translation, J_{GT} , and the solid vibration, J_{SV} : $J_{tot} = J_{GT} + J_{SV}$.

The selective separation of gases through the zeolite pores is based on size exclusion (molecular sieving) and different adsorption of the components (adsorption selective separation). In the case of adsorption selective separation, all components of the targeted mixture are entering the pores of the zeolite. As previously mentioned, the adsorption of the single gases inside the pores depends on the temperature, pressure and component concentration. Therefore, the selectivity varies with the separation conditions. In the case of molecular sieving, only the gas smaller in size is able to enter the pores. Hence, the selectivity is independent on the separation conditions.

Molecular sieving membranes are preferred candi-

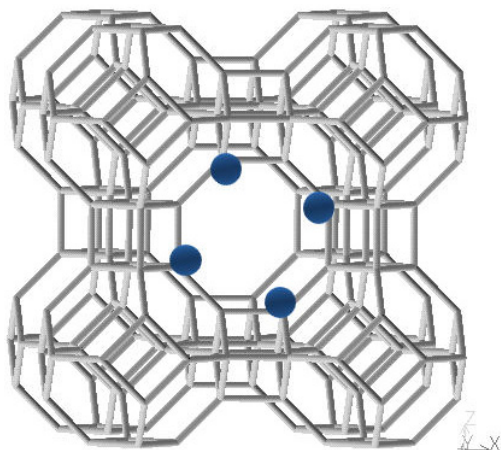


Fig. 4. Illustration of extra framework monovalent cation positions in one window of zeolite A[7].

dates for selective membranes at high temperature and high pressure.

4. Structural, Chemical and Functional Effects of Additives and Substituents in Zeolite

4.1. Modification of the pore size, polarity and adsorption behavior

Zeolite NaA (shown in Fig. 4) is one of the most technically produced zeolites. With a pore size of 0.41 nm and a Si/Al-ratio of 1 for high hydrophilic character, NaA is commercially used for a number of dewatering processes. The small water molecule (0.26 nm) can enter the pores and is adsorbed by the polar sites inside the cages. In technical adsorption columns the wet gases are streaming through the zeolite bed until the zeolite is nearly saturated with water. For desorption the zeolite bed is heated (temperature swing adsorption) or the pressure is decreased (pressure swing adsorption), while the zeolites are swept with a part of the dry gas.

Larger polar gas molecules can enter the cages of zeolite NaA and strongly adsorb inside during the drying of alcohols, amines or H₂S by adsorption technology over long time. Reactive gases like olefins and acetylenic hydrocarbons can be polymerized inside the



Fig. 5. Industrial pilot plant for dewatering of ethanol with NaA-membranes of Fraunhofer IKTS. Reproduced from[15] by permission of John Wiley and Sons Inc.

zeolite pores. By exchanging the extra-framework Na⁺ with the larger K⁺ the open windows of zeolite A are contracted to 0.38 nm (zeolite 3A) minimizing the risk of pore entering by large molecules. Zeolite 3A is the first choice for dehydration of polar and reactive gases by adsorption[12].

By replacing two of the extra-framework Na⁺ by one smaller Ca²⁺ the window is widened to 0.45 nm. The so-called zeolite 5A allows the separation of normal and iso-paraffins and cyclic hydrocarbons because branched and ring compounds are not able to enter the pores. Exchanging the Na⁺ for Ca²⁺ also increases the point charge of the extra-framework cations, changing the adsorption behavior. Therefore, zeolite 5A is used for CO₂ removal prior to the adsorptive air separation and for CO and N₂ adsorption in H₂ production from water gas shift (in combination with carbon).

For filtration on atomic scale, water-containing organic liquids or gaseous mixtures are streamed across the membrane surface. The two relevant processes are called pervaporation (PV) and vapor permeation (VP). Driven by a partial pressure difference, only water is permeating through the narrow zeolite pores. The advantages of the membrane processes are the continuous processing, very low product loss and lower energy consumption. A first industrial plant for the dewatering of ethanol by PV was equipped with NaA membranes prepared on the outside of ceramic tubes by the Japanese company Mitsui Engineering and Shipbuilding Co. Ltd. (Mitsui)[13]. A commercial bio-ethanol dewatering by VP with NaA membranes was first preceded by Bussan Nanotech Research Institute Inc.[14]. In Europe, Inoceramic GmbH (today Fraunhofer IKTS,

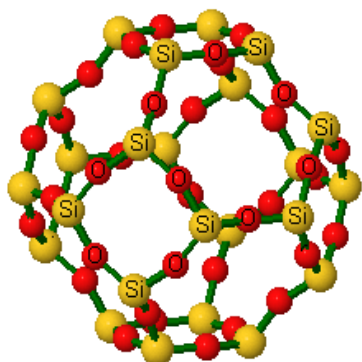


Fig. 6. Al-free SOD-structure.

Hermsdorf branch) in 2007 equipped a first pilot plant for bio-ethanol dewatering by PV with zeolite membranes prepared inside a four channel structure and in 2009 an industrial scale plant[15](see Fig. 5).

Besides ethanol, several other organic solvents like methanol, propanol and higher alcohols, as well as ketones and ethers can be dewatered with NaA membranes. By cation exchange with Ca^{2+} , zeolite 5A membranes can be prepared in order to be permeable also for small organic molecules like methanol.

4.2. Modification of the thermal and hydrothermal stability

The zeolite LTA has narrow pores making the material interesting for gas separating membranes. The high surface charge of the single LTA crystals prevents a defect-free intergrowth. In dewatering processes (PV and VP) remaining narrow mesopores are filled with water. However, these pores are considered as defects in dry gas separation techniques, where defect-free membrane layers with high degree of intergrowth are required[16]. In the presence of water, the hydrothermal stability of LTA is limited to 200°C [17] and there is nearly no tolerance against acetic attacks in liquid solutions. Lowering the Al content would extend the potential application of LTA membranes. Dealumination by steam treatment allows the decrease of the Al content of LTA powders but this approach produces mesopores[18].

Corma *et al.*[19] found a synthesis route for Al-free

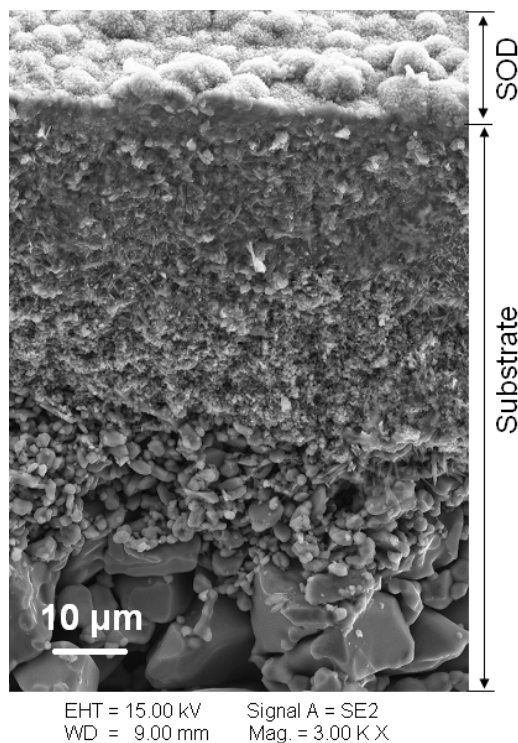


Fig. 7. SEM image of a membrane layer made of sulfur-stabilized SOD.

pure silica LTA. The so-called ITQ-29 was prepared by using a special structure-directing agent (SDA). A very high thermal stability (up to temperature of 800°C) was observed also in the presence of water (2.5 vol%). However, the relatively high viscosity of the synthesis gel complicated the membrane manufacturing[20].

Huang *et al.*[21,22] used a crown ether to prepare an Al-free LTA with $1/3 \text{ Ge}^{4+}$ on the lattice sites of Si^{4+} . Hence, the synthesis conditions and the low surface charge of Al-free LTA enabled the preparation of thin molecular sieving membrane layers on top of porous Al_2O_3 -supports.

Zeolite structures can also be constructed from $[\text{AlO}_4]^{5-}$ - and $[\text{PO}_4]^{3-}$ -tetrahedrons. No extra-framework cations are necessary to make the AIPO-crystals less polar in contrast to the high Al-containing zeolites. A H_2 -selective membrane of AIPO-LTA was prepared by Huang *et al.*[23,24] using a crown ether-SDA. The hydrothermal stability of this material has not been studied yet.

Sodalite is a zeolite structure built only by the β -cages of zeolite LTA (see Fig. 7). The 6-rings are the largest openings with a diameter of 0.28 nm making the material interesting for high selective H₂- and H₂O-separation based on the molecular sieving mechanism. First water and hydrogen selective hydroxo-sodalite (H-SOD, Na₄(Si₃Al₃O₁₂)(OH)) membranes were prepared by Khajavi *et al.*[25] and Xu *et al.*[26]. However, the high Al-content of the material (Si/Al = 1) caused a low hydrothermal stability. Therefore Bibby *et al.*[27] developed Al-free SOD (schematically shown in Fig. 6) by using a SDA-supported synthesis.

Same high hydrothermal stability was found for powder samples as for the Al-free LTA (ITQ-29). Münzer *et al.*[28] crystallized defect-free membrane layers of Al-free SOD on top of porous Al₂O₃ supports. However, during thermal de-templating to empty the SOD cages the layers always cracked. In conclusion, defect-free hydrothermally stable molecular sieves made of SOD membranes cannot be prepared by a SDA-supported synthesis.

The SDA-free synthesis allowed the manufacturing of crack-free membrane as illustrated in Fig. 7. An additional extra-framework Na⁺ is compensated by an extra-framework OH⁻, which is localized in the middle of the SOD cage and stabilizes the SOD structure. The small OH⁻ (0.26 nm) potentially leaves the cage in high thermal and hydrothermal condition causing a collapsing of the SOD structure. The H-SOD synthesis with additional Na₂S causes a partial substitution of the small OH⁻ by the bigger S²⁻ (0.34 nm) or SO₂²⁻ (0.46 nm). These bigger anions are not able to leave the cage leading to a high thermal and hydrothermal stability identical to that of Al-free SOD and LTA (ITQ-29). Molecular sieving behavior was found in H₂-separation tests also at higher temperatures.

5. Conclusion

Membranes made of zeolites are of great interest because of its fixed and open pores in the size of small

molecules inside crystalline structures allowing separation processes under harsh conditions. Zeolite NaA is industrial used for dewatering of organic solvents. Pore size, thermal and hydrothermal stability of the same LTA structure can be tuned by exchange of extra-framework and framework elements. SOD, the β -cages of zeolite LTA is most promising zeolite for H₂ and H₂O-separation. Again separation behavior and thermal and hydrothermal stability can be tuned by exchange of extra-framework and framework elements. So zeolites are prospective materials for creating of membranes with fine-tuned pore sizes, adsorption properties and specific stabilities.

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