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(54) Title: BLOCKING DEFECTS IN MOLECULAR SIEVE MEMBRANES WITH CYCLODEXTRIN

(57) Abstract: The invention provides methods for cyclodextrin treatment of polycrystalline molecular sieve membranes and cyclodextrin-treated molecular sieve membranes. The cyclodextrin treatment can improve the CO₂/CH₄ selectivity of the membrane without causing a large decrease in the CO₂ flux. The invention also provides separation methods employing these cyclodextrin-treated membranes. The molecular sieve membranes may be SAPO-34.



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BLOCKING DEFECTS IN MOLECULAR SIEVE MEMBRANES WITH CYCLODEXTRIN

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U. S. Provisional Application No. 61/250.133, filed October 9, 2009, which is hereby incorporated by reference to the extent not inconsistent with the disclosure herein.

BACKGROUND

[0002] Zeolites are largely composed of Si, Al and O and have a three-dimensional microporous crystal framework structure largely of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral units. To balance negative charge due to the incorporation of Al atoms in the framework, cations are incorporated into the cavities and channels of the framework. Acid hydrogen forms of zeolites have protons that are loosely attached to the framework structure. The cages, channels and cavities created by the crystal framework can permit separation of mixtures of molecules based on their effective sizes.

[0003] Different zeolites may have different Si/Al ratios and the tetrahedra can also be isostructurally substituted by other elements such as B, Fe, Ga, Ge, Mn, P, and Ti. In an extreme case, zeolite molecular sieves may have a Si/Al ratio approaching infinity. Silica molecular sieves do not have a net negative framework charge, exhibit a high degree of hydrophobicity, and have no ion exchange capacity. Silicalite-1, and silicalite-2, and Deca-dodecasil 3R (DD3R) are examples of silica molecular sieves.

[0004] Aluminophosphate (AIPO) molecular sieves are largely composed of Al, P and O and have three-dimensional microporous crystal framework structure largely of $[\text{PO}_4]^{3-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral units. Silicoaluminophosphate (SAPO) molecular sieves are largely composed of Si, Al, P and O and have a three-dimensional microporous crystal framework structure largely of $[\text{PO}_4]^{3-}$, $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$ tetrahedral units. Molecular sieve framework structures are discussed in more

detail by Baerlocher et al. (Baerlocher, Ch., et al., 2001, Atlas of Framework Structures Types, 5th revised ed., Elsevier, Amsterdam).

[0005] Transport through a zeolite-type or molecular sieve membrane can be described by several parameters. As used herein, a membrane is a semi-permeable barrier between two phases that is capable of restricting the movement of molecules across it in a very specific manner. As used herein, the flux, J_i , through a membrane is the number of moles of a specified component i passing per unit time through a unit of membrane surface area normal to the thickness direction. The permeance or pressure normalized flux, P_i , is the flux of component i per unit transmembrane driving force. For a diffusion process, the transmembrane driving force is the gradient in chemical potential for the component (Kärger, J. Ruthven, D.M., Diffusion in Zeolites, John Wiley and Sons: New York, 1992, pp. 9-10). The selectivity of a membrane for components i over j , $S_{i/j}$ is the permeance of component i divided by the permeance of component j . The ideal selectivity is the ratio of the permeances obtained from single gas permeation experiments. The actual selectivity (also called separation selectivity) for a gas mixture may differ from the ideal selectivity.

[0006] For two gas components i and j , a separation selectivity $S_{i/j}$ greater than one implies that the membrane is selectively permeable to component i . If a feedstream containing both components is applied to one side of the membrane (the feed side), the permeate stream exiting the other side of the membrane (the permeate side) will be enriched in component i and depleted in component j . The greater the separation selectivity, the greater the enrichment of the permeate stream in component i .

[0007] Transport of gases through zeolite pores can be influenced by several factors. A model proposed by Keizer et al. (J. Memb. Sci., 1998, 147, p. 159) has previously been applied to SAPO-34 membranes (Poshusta et al., AIChE Journal, 2000, 46(4), pp 779-789). This model states that both molecular sizes relative to the zeolite pore size and the relative adsorption strengths determine the faster permeating species in a binary mixture. This gives rise to three separation regimes where both components are able to diffuse through the molecular sieve pores. In the first region, both molecules have similar adsorption strengths, but one is larger

and its diffusion is restricted due to pore walls. In the first region, the membrane is selective for the smaller molecule. In region 2, both molecules have similar kinetic diameters, but one adsorbs more strongly. In region 2, the membrane is selective for the strongly adsorbing molecule. In region 3, the molecules have significantly different diameters and adsorption strengths. The effects of each mechanism may combine to enhance separation or compete to reduce the selectivity.

[0008] Transport of gases through a crystalline molecular sieve membrane can also be influenced by any “nonzeolite pores” in the membrane structure. The contribution of nonzeolite pores to the flux of gas through a zeolite-type membrane depends on the number, size and selectivity of these pores. For polycrystalline molecular sieve membranes, some flow is expected through intercrystalline regions. If the nonzeolite pores are sufficiently large, transport through the membrane can occur through Knudsen diffusion or viscous flow. For MFI zeolite membranes, it has been reported that nonzeolite pores that allow viscous and Knudsen flow decrease the selectivity (Poshusta, J.C. et al., 1999, “Temperature and Pressure Effects on CO₂ and CH₄ permeation through MFI Zeolite membranes,” J. Membr. Sci., 160, 115).

[0009] Various post-treatment methods have been used to decrease flow through membrane defects and increase the selectivity. Gavalas and co-workers blocked intercrystalline gaps [6] by impregnating ZSM-5 membranes with liquid 1,3,5-triisopropylbenzene (TIPB), followed by high temperature coking. The kinetic diameter of TIPB (0.84 nm) is larger than the pore aperture of ZSM-5 crystals (0.55 nm) and therefore did not enter the zeolite channels. The n-butane/i-butane ideal selectivity at 458 K increased from 9.7 to 107, but the flux dropped substantially, indicating that some flow through the zeolite crystals were also blocked. Tsapatsis et al. [7, 8] sealed defects by dip-coating MFI membranes in a mesoporous silica sol. After drying, the mesoporous silica layer that formed on top of the membranes cracked and could be easily removed with compressed air. The silica sol that penetrated into the defects was not removed, and the defects were selectively blocked. The selectivity of *p*-xylene/*o*-xylene was increased from 12 to 30~300. However, significant flux reduction was also observed.

[0010] Matsuda et al. [9] soaked silicalite membranes in a silicone rubber solution, followed by drying at room temperature. A diluted polymer solution was used to avoid blocking the zeolite channels. The separation factor of ethanol/water was increased from 51 to 125 without sacrificing ethanol flux. This improvement was explained by closing the intercrystalline boundaries of the membrane. Nomura et al. [10] used chemical vapor deposition (CVD) to modify silicalite membranes; they counter-diffused tetraethoxy orthosilicate (TEOS) and O₃. The TEOS molecule is too large to penetrate into zeolitic pores, but the intercrystalline regions were filled with silica as the ozone oxidized TEOS. The separation selectivity for an n/i-butane mixture increased from 9.1 to 87.8 at 288 K but the flux was also significantly reduced as some of the zeolite pores were blocked. A similar procedure was reported by McHenry et al. [11], who used low-temperature, counter-diffusion CVD to block defects in zeolite membranes. Silicon sources, such as tetramethoxysilane, tetraethoxysilane, and ozone were introduced from different sides of the membrane and silica formed inside the membrane defects. The separation properties of the membrane were greatly improved but fluxes also decreased.

[0011] Zhang et al. [12] used counter-diffusion chemical liquid deposition (CLD) to selectively patch defects in silicalite membranes; dodecyltrimethoxysilane formed a protective layer on the membrane surface prior to the CLD treatment. Tetraethoxy orthosilicate and (3-chloropropyl) triethoxysilane in an organic solvent and an aqueous solution of a basic catalyst were introduced on opposite sides of the membrane, and the hydrolysis and condensation products at the organic/aqueous interface (silsesquioxane/silicate hybrid) reportedly closed the defects. The silsesquioxane/silicate hybrid was reported to deposit only at the pore-mouth of the defects, and the defect sizes reportedly decreased to 1.3 nm. The separation factor for a 50/50 n/i-butane-gas mixture increased from 4.4 to 35.8, and the separation factor of a CO₂/N₂ gas mixture increased from 1 to around 15, while the CO₂ flux only dropped by 1/3. These procedures, although they increased selectivity, are complex and they decreased fluxes significantly.

[0012] Other membrane treatments have been used to modify molecular sieve membrane selectivity. U.S. 2006/0079725 to Li et al. describes modified molecular membranes with improved CO₂/CH₄ selectivity, wherein the membranes are

modified by adsorption of a modifying agent within and/or on the membrane. Published PCT Application WO 2008/106647 to the Regents of the University of Colorado describes adsorption of a swelling agent within the pores of molecular sieve crystals to modify transport through the membrane.

[0013] Modification of ceramic membranes has also been reported. Krieg et al. describes modification of ceramic membranes by impregnation with β -cyclodextrin polymer (Krieg, H.M. et al., J. Membr. Sci., 164(2000) 177-185). The ceramic membranes were reported to consist mainly of Al_2O_3 and Zr_2O_3 . Takaba et al. report cyclodextrin-modified ceramic membranes (Ind. Eng. Chem. Res. 2003, 42, 1243-1252). The cyclodextrins were reported to be directly immobilized to the surface of a $\text{TiO}_2/\text{Al}_2\text{O}_3$ ceramic nanofiltration membrane, with a cross-linking agent being used to obtain further stabilization of the cyclodextrin layer.

BRIEF SUMMARY

[0014] In one aspect, the invention relates to cyclodextrin treatment of polycrystalline molecular sieve membranes. In an embodiment, the cyclodextrin treatment is capable of improving the CO_2/CH_4 selectivity of the membrane, especially when the pressure across the membrane is on the order of several MPa. In an embodiment, the selectivity is improved without causing a large decrease in CO_2 flux. The separation of CO_2 from CH_4 is important in natural gas processing because CO_2 reduces the energy content of natural gas. Many natural gas wells contain high concentrations of CO_2 (as high as 70%). It is desirable to remove most of this CO_2 before the natural gas is shipped and used in order to minimize corrosion in the pipelines and increase the heating value of the natural gas. To increase the flux across the membrane, it is desirable to use a relatively high pressure differential across the membrane. In industrial gas separation processes, the pressure drop across the membrane can be several MPa. For example, in the natural gas industry the transmembrane pressure drop is about 6-7 MPa.

[0015] In an embodiment, the invention provides a method of treating a calcined molecular sieve membrane comprising zeolite pores and non-zeolite pores, the method comprising the steps of:

- a) preparing a treatment solution comprising cyclodextrin molecules and a solvent;
- b) contacting the membrane with the treatment solution; and
- c) removing solvent from the membrane

wherein the outside diameter of the cyclodextrin molecules is larger than the characteristic zeolite pore size. The molecular sieve membrane may be referred to as a crystalline or polycrystalline membrane. Some or all of the treatment steps may be repeated. For example, step b) may be repeated, contacting the membrane with a quantity of previously unused solution in each iteration, before performing step c). The cyclodextrin (CD) molecules may be adsorbed within the non-zeolite pores. The cyclodextrin molecule may be native or derivatized, and may have from 6-20 glucose or glucopyranose units. The CD molecule may be native or derivatized β -CD. Following treatment, the number of moles of CD per unit volume of molecular sieve membrane may be greater than 1×10^{-7} moles/mm³, greater than 5×10^{-7} moles/mm³, greater than 1×10^{-6} moles/mm³ or from 5×10^{-7} to 1×10^{-5} moles/mm³. Measured in terms of surface area, the number of moles of CD per nominal surface area of the support may be greater than 5×10^{-10} moles/mm², greater than 1×10^{-9} moles/mm², greater than 5×10^{-9} moles/mm², from 5×10^{-10} to 1×10^{-7} moles/mm² or from 1×10^{-9} moles/mm² to 1×10^{-7} moles/mm².

[0016] Typically, the treatment solution will at least partially penetrate the pores of the molecular sieve membrane. However, when the cyclodextrin molecules are significantly larger than the zeolite pores, cyclodextrin molecules will not be able to enter the zeolite pores and will be restricted to larger non-zeolite pores.

[0017] In an embodiment, the cyclodextrin molecules adsorb within the non-zeolite pores of the membrane during the treatment process. In an embodiment, the treatment process does not involve polymerization of the cyclodextrin molecules subsequent to their adsorption within the membrane. In another embodiment, the treatment process does not involve decomposition of the cyclodextrin molecules, although the cyclodextrin molecules may be decomposed following treatment to remove them from the membrane.

[0018] The characteristic pore diameter of the molecular sieve may be less than or equal to 1 nm, 0.75 nm, or 0.5 nm, from 0.25 to 1 nm, or from 0.3 to 0.8 nm. In different embodiments, the molecular sieve is selected from the group consisting of SAPO-34, AIPO-18, DDR, zeolite A, ZSM-5, silicalite-1, and TS-1.

[0019] A single species of cyclodextrin molecule or combinations of cyclodextrin species may be used. In an embodiment, the cyclodextrin is selected from the group consisting of α , β or γ cyclodextrins or combinations thereof. In another embodiment, the cyclodextrin is a α or β cyclodextrin or combinations thereof. In another embodiment, the cyclodextrin may be a cyclodextrin with more than 7 glucopyranose units. In another embodiment, the cyclodextrin may be a derivatized cyclodextrin such as a derivatized α , β or γ cyclodextrin.

[0020] The solvent may be any liquid capable of dissolving the cyclodextrin. In an embodiment, the solvent is water or an aqueous solution. In different embodiments, the concentration of the cyclodextrin is from 0.5-5 wt%, 0.75-3 wt% or 1-2 wt%.

[0021] In an embodiment the solvent may be removed from the membrane through drying. In an embodiment, the drying temperature is less than the decomposition temperature of the cyclodextrin molecules. In an embodiment, the zeolite membrane is stored at a temperature high enough to prevent adsorption of water from the atmosphere. In an embodiment, the zeolite membrane is stored at a temperature from 200 °C to less than 290 °C.

[0022] Typically an effective amount of the cyclodextrin (CD) is introduced into the membrane. The quantity of cyclodextrin introduced into the membrane may be measured via flow chemisorption techniques such as temperature programmed oxidation. In different embodiments, the moles of CD per cubic millimeter of molecular sieve membrane is greater than 1×10^{-7} , greater than 5×10^{-7} , from 1×10^{-7} to 1×10^{-5} , or from 5×10^{-7} to 1×10^{-5} .

[0023] In another aspect, the invention provides cyclodextrin treated molecular sieve membranes. The molecular sieve membrane may be referred to as a crystalline or polycrystalline membrane. In an embodiment, the molecular sieve membranes are modified by adsorption of cyclodextrin molecules within the non-

zeolite pores of the polycrystalline membrane according to the methods of the invention. In an embodiment, the cyclodextrin treated molecular sieve membranes are supported membranes. In an embodiment, the cyclodextrin treated molecular sieve membranes of the invention have improved CO₂/CH₄ selectivity as compared to the CO₂/CH₄ selectivity of the membrane prior to cyclodextrin treatment.

[0024] In another aspect, the invention relates to transport of chemical species through a molecular sieve membrane comprising interlocking crystals of the molecular sieve. In a particular aspect of the invention, transport of a first component through the membrane is controlled at least in part through cyclodextrin treatment of the membrane.

[0025] In an embodiment, the invention provides a method for reducing the transport of a component through a molecular sieve membrane comprising zeolite pores and non-zeolite pores, wherein the method comprises the step of adsorbing a sufficient quantity of cyclodextrin molecules in the non-zeolite pores to reduce transport of the component through the non-zeolite pores of the membrane. The transport is reduced as compared to the transport prior to cyclodextrin treatment. In an embodiment, the size of the cyclodextrin molecule is selected so that it is larger than the characteristic zeolite pore size of the molecular sieve membrane. In different embodiments, the transport may be measured by the flux of the component through the membrane or the permeance of the component at a given pressure drop

[0026] At least one additional component may also transported be through the molecular sieve membrane with the reduction in transport of one component being greater than the other component. In different embodiments, the transport may be measured by the flux of the component through the membrane or the permeance of a given component at a given pressure drop. In an embodiment, the percentage reduction in transport may be calculated as $100 \times (1 - \frac{\text{the extent of transport after treatment}}{\text{the extent of transport before treatment}})$. For example, the percentage reduction in transport may be calculated as $100 \times (1 - \frac{\text{permeance after membrane treatment}}{\text{permeance before membrane treatment}})$. In an embodiment, the percentage transport reduction for one component is at least twice that of the other. In an embodiment, the cyclodextrin treatment decreases the amount the flux or the

permeance of the other component by less than or equal to 30%, 20%, or 10%. In different embodiments, the pressure differential for which the reduction in transport is measured is from 0.1 MPa to 10 MPa, from 0.3 MPa to 7 MPa, from 1 MPa to 5 MPa, from 2 MPa to 4 MPa, or from 3 MPa to 10 MPa. The pressure at the permeate side of the membrane may be ambient pressure (e.g. about 84 kPa). These performance parameters may be obtained for a 50/50 (molar %) mixture of the two components at ambient temperature (e.g. a temperature in the range 20-25 °C or 293-300 K or at 295K).

[0027] In an embodiment, both CO₂ and CH₄ are transported through the membrane, and cyclodextrin treatment produces a reduction in the amount of CH₄ being transported through the membrane. In an embodiment, the CO₂/CH₄ selectivity of the membrane is improved at a particular pressure. In an embodiment, the CO₂/CH₄ selectivity may be improved from 10% to 150%, depending on the defects initially present in the membrane. In an embodiment, the cyclodextrin treatment decreases the amount of CO₂ flux by less than or equal to 30%, 20%, or 10%. These performance parameters may be obtained for a 50/50 (molar %) mixture of the two components at ambient temperature (e.g. a temperature in the range 20-25 °C or 293-298 K or at 295K).

[0028] In an embodiment, the invention provides a method for separating molecules of a first substance from molecules of a second substance, the method comprising the steps of:

- a. providing a molecular sieve membrane, the membrane comprising molecular sieve pores and non-molecular sieve pores and having a feed side and a permeate side wherein a sufficient quantity of cyclodextrin molecules is present within the non-molecular sieve pores of the membrane to improve the selectivity of the membrane to the first substance over the second substance ;
- b. providing a feed stream including molecules of the first and second substances at the feed side of the membrane;
- c. providing a driving force sufficient for permeation of molecules of the first substance through the membrane, thereby producing a permeate stream enriched in molecules of the first substance

wherein the diameter of the cyclodextrin molecules is larger than the characteristic zeolite pore size. The molecular sieve membrane may be referred to as a crystalline or polycrystalline membrane. The cyclodextrin (CD) molecules may be adsorbed within the non-zeolite pores. The cyclodextrin molecule may be native or derivatized, and may have from 6-20 glucose or glucopyranose units. The CD molecule may be native or derivatized β -CD. The number of moles of CD per unit volume of molecular sieve membrane may be greater than 1×10^{-7} moles/mm³, greater than 5×10^{-7} moles/mm³, greater than 1×10^{-6} moles/mm³ or from 5×10^{-7} to 1×10^{-5} moles/mm³. Measured in terms of surface area, the number of moles of CD per nominal surface area of the support may be greater than 5×10^{-10} moles/mm², greater than 1×10^{-9} moles/mm², greater than 5×10^{-9} moles/mm², from 5×10^{-10} to 1×10^{-7} moles/mm² or from 1×10^{-9} moles/mm² to 1×10^{-7} moles/mm². The improvement in selectivity may be 10-150%, 5-75%, 20-75%, 20-150%, 50-150% or least 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% or 100%. The percentage transport reduction for the second component may be at least twice that the first component. The cyclodextrin treatment may decrease the amount the flux or the permeance of the first component by less than or equal to 30%, 20%, or 10%. The pressure differential for which the reduction in transport is measured may be from 0.1 MPa to 10 MPa, from 0.3 MPa to 7 MPa, from 1 MPa to 5 MPa, from 2MPa to 4 MPa, or from 3 MPa to 10 MPa. The pressure at the permeate side of the membrane may be ambient pressure (e.g. about 84 kPa). These performance parameters may be obtained for a 50/50 (molar %) mixture of the two components at ambient temperature (e.g. a temperature in the range 20-25 °C or 293-300 K or at 295K). In an embodiment, the first substance is CO₂, the second substance is CH₄ and the molecular sieve membrane is a SAPO-34 membrane.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] Figure 1: Selectivity (1a) and fluxes (1b) of a 50/50 CO₂/CH₄ mixture as a function of pressure drop for SAPO-34 membrane M6 at 295 K before and after β cyclodextrin treatment.

[0030] Figure 2: Selectivity (2a) and fluxes (2b) of a 50/50 CO₂/CH₄ mixture as a function of pressure drop for SAPO-34 membrane M7 at 295 K before and after β cyclodextrin treatment.

[0031] Figure 3: Selectivity of a 50/50 CO₂/CH₄ mixture as a function of pressure drop for SAPO-34 membrane M8 at 295 K before and after β cyclodextrin treatment.

[0032] Figure 4: Selectivity (4a) and fluxes (4b) of a 50/50 CO₂/CH₄ mixture as a function of pressure drop for SAPO-34 membrane M9 at 295 K before and after cyclodextrin treatment.

[0033] Figure 5: Selectivity (5a) and permeance (5b) of a 50/50 CO₂/CH₄ mixture as a function of pressure drop for SAPO-34 membrane M10 at 295 K before and after β-cyclodextrin treatment.

[0034] Figure 6: Selectivity (6a) and fluxes (6b) of a 50/50 CO₂/CH₄ mixture as a function of pressure drop for SAPO-34 membrane M11 on an alumina support at 295 K before and after β-cyclodextrin treatment

[0035] Figure 7: Single-component CF₄ permeance and binary CH₄ permeance for SAPO-34 membrane M9 at 295 K before and after cyclodextrin treatment a) flux; b) permeance.

[0036] Figure 8 Permporometry measurements with i-butane and benzene for a SAPO-34 membrane M9 before and after CD deposition.

[0037] Figure 9: Temperature programmed oxidation of a cyclodextrin-treated SAPO-34 membrane.

DETAILED DESCRIPTION

[0038] Molecular sieves can be classified as small, medium, or large-pore molecular sieves based on the size of the largest oxygen rings in the structure. Structures where the largest ring contains 8 or fewer oxygen atoms are typically considered small-pore molecular sieves. Small pore molecular sieves include zeolite A, silicoaluminophosphate (SAPO)-34, and Deca-dodecasil 3R (DDR). In an embodiment, the molecular sieve has a small pore-size structure.

[0039] As used herein, “zeolite pores” or “molecular sieve pores” are pores formed by the crystal framework of a zeolite-type or molecular sieve material. The zeolite pore size(s) can be determined from the crystal structure. As used herein

“nonzeolite pores” or “non-molecular sieve pores” are pores not formed by the crystal framework. Intercrystalline pores are an example of nonzeolite pores. As used herein, the characteristic pore size of the zeolite is the maximum size of the pores formed by the crystal framework.

[0040] The molecular sieve membranes used with the invention comprise interlocking crystals of the molecular sieve. In an embodiment, the membranes of the invention may be a supported membrane having a molecular sieve component and a support component, with the molecular sieve component of the membrane consisting essentially of synthetic molecular sieve crystals. In different embodiments, synthetic molecular sieve crystals comprise 90-100 wt%, 95-100 wt% or 98-100 wt% of the molecular sieve component of the calcined membrane. The molecular sieve component of the membrane is distinguished from a natural zeolite, which typically includes non-zeolite components. The molecular sieve component of the membrane is also structurally distinct from a single zeolite particle or a packed bed of zeolite particles.

[0041] In an embodiment, the molecular sieve membrane may be SAPO-34 (CHA), aluminophosphate-18 (AIPO-18) (CHA), Deca-Dodacasil 3R (DDR), zeolite A (LTA), Zeolite Socony Mobil-5 (ZSM-5) (MFI), silicalite-1 (MFI), Titanium Silicalite (TS-1) (MFI), zeolite X or Y (FAU), AIPO-5 or SAPO-5 (AFI), mordenite (MOR), ferrierite (FER), MEL or ZSM-11, zeolite P (KFI), sodalite (SOD), or a mixed tetrahedral-octahedral oxides (Englehard TitanoSilicate ETS-4 and ETS-10). The molecular sieve membranes may be isostructurally substituted by other elements such as B, Fe, Ga, Ge, Mn, P, and Ti (e.g. B-ZSM).

[0042] In an embodiment, the molecular sieve membrane may be SAPO-34 (CHA, characteristic pore size approximately 0.38 nm), AIPO-18 (AEI, characteristic pore size approximately 0.38 nm), zeolite A (LTA, characteristic pore size approximately 0.4 nm), ZSM-5 (MFI), silicalite-1 (MFI, characteristic pore size approximately 0.55 nm), or zeolite Y (FAU, characteristic pore size approximately 0.73 nm).

[0043] Some molecular sieve membranes, including SAPOs, can exhibit cation exchange properties. The excess negative charge in the lattice may be compensated by protons or by compensating cations located in the cavities of the

structural framework. Acid hydrogen forms of molecular sieve membranes (e.g. H-SAPO-34) have protons that are loosely attached to their framework structure in lieu of inorganic compensating cations. In an embodiment, the molecular sieve membranes used in the invention are in acid hydrogen form.

[0044] Molecular sieve membranes may be grown through in-situ crystallization on a porous support to form a supported membrane. As used herein, a supported membrane is a membrane attached to a support. In an embodiment, the methods and devices of the invention may utilize supported molecular sieve membranes. Gels for forming molecular sieve crystals are known to the art, but preferred gel compositions for forming membranes may differ from preferred compositions for forming loose crystals or granules. The preferred gel composition may vary depending upon the desired crystallization temperature and time.

[0045] In an embodiment, the molecular sieve membrane may be formed by providing a porous support, contacting the porous support with a molecular sieve-forming gel comprising an organic templating agent, heating the porous support and molecular sieve forming gel to form a molecular sieve layer at least in part on the surface of the porous support; and calcining the molecular sieve layer to remove the template. For some types of molecular sieves, it may be desirable to prepare the porous support by “seeding” it with molecular sieve crystals prior to contacting the support with the molecular sieve-forming gel. The term “templating agent” or “template” is a term of art and refers to a species added to the synthesis media to aid in and/or guide the polymerization and/or organization of the building blocks that form the crystal framework. The membranes may be calcined prior to cyclodextrin treatment.

[0046] SAPO crystals can be synthesized by hydrothermal crystallization from a reaction mixture containing reactive sources of silica, alumina, and phosphate, and an organic templating agent. Techniques for synthesizing SAPO membranes are described in U.S. Patent 7,316,727 to Falconer et al., U.S. Published Patent Applications US 2007/0265484 to Li et al. and US 2008/0216650 to Falconer et al. and references [1]-[5].

[0047] Cyclodextrins are macrocyclic oligosaccharides connected by α -1,4 linkages, some of which may be characterized as having the shape of a doughnut-shaped truncated cone. As used herein, the term cyclodextrin also includes cyclodextrin derivatives. The three main members of the cyclodextrin family, composed of six, seven and eight glucose (glucopyranose) units, are α -, β -, and γ -CD. These CDs have a truncated conical shape, a hydrophilic exterior and a hydrophobic cavity created by the inward-directed H3 and H5 atoms of the glucose units. These are bulky molecules with approximate dimensions as follows: 1.5-1.8 nm outside diameters, 0.45-0.75 nm cavities and 0.8nm thickness. Table 1 lists several properties of cyclodextrins, some of which are provided by references 14 and 15 [14, 15].

Table 1. Properties of cyclodextrins (CDs)

	α -CD	β -CD	γ -CD
Number of Glucose units	6	7	8
Molecular weight	973	1135	1297
Cavity diameter (nm)	0.47-0.53	0.60-0.66	0.75-0.83
Approximate outside diameter (nm)	1.52	1.66	1.77
Cavity height (nm)	0.79	0.79	0.79
Cavity volume (mL/mol)	174	262	472
Solubility in water at room temperature (g/100 mL)	14.5	1.85	23.2
Melting/Decomposition T (K)	551	563	>573

[0048] Larger cyclodextrins are also known to the art and include δ -CD, ϵ -CD, ξ -CD, η -CD, and θ -CD. The larger CDs are not regular cylinder shaped structures, but are collapsed with a real cavity even smaller than in γ -CD [15]. Cyclodextrins, especially larger cyclodextrins, may be referred to in terms of their polymerization degree or number of glucopyranose units. In different embodiment, number of glucose or glucopyranose units may be from 6 to 20.

[0049] A number of cyclodextrin derivatives have been synthesized. The following CDs have been produced industrially: methylated CDs (RAMEB=randomly methylated β -CD); hydroxyalkylated CDs ((hydroxypropyl- β -CD and hydroxypropyl

γ -CD), acetylated CDs (acetyl- γ -CD), reactive CDs (chlorotriazinyl β -CD) and branched CDs (glucosyl- and maltosyl- β -CD) [15]. In different embodiments, the functional group on the derivative may be hydrophilic or hydrophobic.

[0050] In an embodiment, the outer diameter and height of the cyclodextrin is larger than the characteristic zeolite pore size of the molecular sieve crystals forming the molecular sieve membrane. In an embodiment, the outer diameter and/or height of the cyclodextrin may be selected so that it is smaller than at least some of the non-zeolite pore dimensions in the molecular sieve (thereby allowing entry of the cyclodextrin within the non-zeolite pores). In an embodiment, the outer diameter and/or height of the cyclodextrin may be smaller than the dimensions of the non-zeolite pores to be filled by a significant amount (e.g. a factor of 2-3).

[0051] In an embodiment, the treatment solution comprises cyclodextrin molecules and water. In such a case, the cyclodextrin may be selected at least in part based on its water solubility. If the concentration of cyclodextrin in the solution is too high, permeation through the zeolite pores may be blocked. The concentration of cyclodextrin in the solution may be from 0.25-10 wt%, 0.25-5 wt%, 0.5-5 wt%, 0.25 to 2 wt%, 0.75% to 3 wt%, or from 1% to 2 wt% .

[0052] The cyclodextrin treatment may take place at room temperature (approximately 290-300 K). In another embodiment, the treatment with the cyclodextrin solution takes place at a temperature from 290 K to 373K or from 290 to 323K.

[0053] In an embodiment, the cyclodextrin treatment may take place at ambient pressure. In another embodiment, a pressure differential may be applied across the membrane. In different embodiments the pressure differential is greater than zero and less than 1 MPa, from 0.1 to 0.7 MPa, or from 0.2 to 0.6 MPa.

[0054] The membrane is typically contacted with the cyclodextrin solution for sufficient time to produce improved separation selectivity or reduced transport of a particular component through the membrane. In different embodiments, the treatment time may be from 5 min to 4 hours, from 15 min to 4 hours, from 15 min to 3 hours, from 15 min. to 2 hours, from 15 min to 1 hour, from 30 min to 4 hours, from 30 min. to 3 hours, from 30 min to 2 hours or from 30 min to 1 hour.

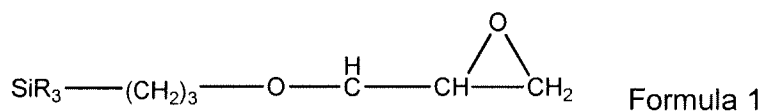
[0055] In an embodiment, the treatment process allows adsorption of the cyclodextrin molecules to occur within the non-zeolite pores. Adsorption of the modifying agent within the membrane may be through chemisorption, physisorption, or a combination thereof. In an embodiment, adsorption of the cyclodextrin molecules within the zeolite membrane is a chemisorption process which may be reversed by heating the membrane above the decomposition temperature of the cyclodextrin. In an embodiment, the original membrane permeance and selectivity may be recovered upon heating the membrane to a temperature above the decomposition temperature of the cyclodextrin.

[0056] In an embodiment, the cyclodextrin molecules are native (nonderivatized) and do not require a linker in order to form a sufficiently strong interaction with the interior of the non-zeolite pores. In an embodiment, a linker may be used to connect the cyclodextrin and the zeolite. In different embodiments, the linker may be $-(CH_2)_n-$, $-(HCCH)_n-$, $-O-$, $-S-$, $-SO-$, $-SO_2-$, $-SO_3-$, $-OSO_2-$, $-NR^2-$, $-CO-$, $-COO-$, $-OCO-$, $-OCOO-$, $-CONR^3-$, $-NR^4CO-$, $-OCONR^5-$, $-NR^6COO-$, or $-NR^7CONR^8-$; where each of $R^2 - R^8$ is independently hydrogen or C_1 - C_{10} alkyl; and n is an integer selected from the range of 1 to 10.

[0057] In an embodiment, the cyclodextrin may be derivatized to improve attachment of the cyclodextrin molecules to the zeolite; in different embodiments, the cyclodextrin may be functionalized with $-OH$, $-NH_2$, $-NH$, or $-COOH$ functional groups. In another embodiment, a cationic CD can be used. Li et al. (2009, Water Science and Technology, 60(2), 329-337 describe formation of a cationic beta-CD which can then bind to zeolite surfaces through ion exchange. The cationic CD was reported to be formed through reaction of hydroxyl groups of the beta-CD with the epoxy group of 2,3 epoxypropyltrimethylammonium chloride (ETMAC) in the presence of NaOH.

[0058] In another embodiment, the surface of the zeolite can be modified to bind the cyclodextrin molecules more strongly. Various methods have been described in the literature for immobilizing cyclodextrins to solid inorganic surfaces. For example, US Patent 4,539,399 describes attachment of cyclodextrins to silica gel through reaction of a silane with the silica gel and then reaction of this product

with a cyclodextrin. This patent describes a first group of linkage materials described by the formula:



in which each R is selected from the group consisting of methoxy, ethoxy, lower alkyl, Cl or Br. Not all of the R's need be the same. Exemplary compounds are 3-glycidopropyl trimethoxy silane; 3-glycidopropyl dimethylchloro silane; and 3-glycidopropyl triethoxy silane. Direct coupling of cyclodextrin to silanized silica gel using a sodium hydride treated cyclodextrin was reported. In an embodiment of the present invention, the molecular sieve surface is modified by reaction with a silane molecule, the silane molecule also including a functional group which binds the cyclodextrin molecule.

[0059] After treating the membrane with the cyclodextrin solution, the membrane may be dried to remove solvent. When the solvent is water, the membrane may be dried at a temperature above the boiling point of water for at least some portion of the drying process. A two part drying procedure may be used, with the first part of the procedure taking place at a lower temperature (e.g. room temperature) and the second part of the procedure at a higher temperature.

[0060] The amount of cyclodextrin present within the membrane can be described in several ways. In different embodiments, the amount of cyclodextrin present within the molecular membrane can be referenced to the mass of the molecular sieve membrane, to the nominal volume of the molecular sieve membrane, or to the surface area of the support used to form the membrane. As used herein, the nominal volume of the membrane is the volume as determined from the membrane dimensions (for example thickness and length). In an embodiment, the number of moles of CD per unit volume of molecular sieve membrane is greater than 1×10^{-7} moles/mm³, greater than 5×10^{-7} moles/mm³, greater than 1×10^{-6} moles/mm³ or from 5×10^{-7} to 1×10^{-5} moles/mm³. In another embodiment, the number of moles of CD per nominal surface area of the support is greater than 5×10^{-10} moles/mm², greater than 1×10^{-9} moles/mm², greater than 5×10^{-9} moles/mm², from 5×10^{-10} to 1×10^{-7} moles/mm² or from 1×10^{-9} moles/mm² to 1×10^{-7} moles/mm².

[0061] Effective amounts of cyclodextrin for reduction of the effect of non-zeolite pores on transport through the membrane can be determined by testing of similar membranes containing different amounts of cyclodextrin. If the initial transport properties of the membrane can be recovered after removal of the cyclodextrin, the same membrane can also be tested with different amounts of cyclodextrin. In an embodiment, two components are transported through the molecular sieve membrane, and the amount of cyclodextrin introduced in the membrane is sufficient to reduce transport of the one component without unduly reducing transport of the other component. In an embodiment, the percentage transport reduction for one component is at least twice that of the other component. In an embodiment, the cyclodextrin treatment decreases the amount the flux or the permeance of the other component by less than or equal to 30%, 20%, or 10%. In different embodiments, the pressure differential for which the reduction in transport is measured is from 0.1 MPa to 10 MPa, from 0.3 MPa to 7 MPa, from 1 MPa to 5 MPa, from 2MPa to 4 MPa, or from 3 MPa to 10 MPa. The pressure at the permeate side of the membrane may be ambient pressure (e.g. about 84 kPa). These performance parameters may be obtained for a 50/50 (molar %) mixture of the two components at ambient temperature (e.g. a temperature in the range 20-25 °C or 293-300 K or at 295K).

[0062] The use temperature of the modified membrane may be influenced by conditions at which the cyclodextrin begins to decompose. In an embodiment, the use temperature is below the decomposition temperature of the cyclodextrin(s).

[0063] Polycrystalline SAPO-34 zeolite membranes have been shown to have high selectivities for CO₂/CH₄ separations, even at high pressures [1-5]. The selectivity of the SAPO-34 membranes decreased as the feed pressure increased. The decrease in selectivity is believed to result from permeation through defects (intercrystalline regions) by Knudsen diffusion and viscous flow increasing proportionally more at higher pressures than permeation through the SAPO-34 pores. The CO₂ adsorption isotherm indicates that the flux through the SAPO-34 pores is not expected to increase linearly with pressure because the pores approach saturation loading (Adolfo M. Avila, Hans H. Funke, Yanfeng Zhang, John

L. Falconer, Richard D. Noble, *Journal of Membrane Science*, Volume 335, Issues 1-2, 15 June 2009, Pages 32-36).

[0064] In different embodiments, the transport through the membrane may be measured by the flux of the component through the membrane at a given feed pressure or the permeance of a given component at a given pressure drop. In an embodiment, the percentage reduction in transport may be calculated as $100 \times (1 - \frac{\text{the extent of transport after treatment}}{\text{the extent of transport before treatment}})$. For example, the percentage reduction in transport may be calculated as $100 \times (1 - \frac{\text{permeance after membrane treatment}}{\text{permeance before membrane treatment}})$. In an embodiment, the percentage transport reduction for component 1 is at least twice that of component 2.

[0065] The transport of a component through the membrane may be affected by whether the component changes the dimensions of the molecular sieve crystals. For MFI membranes, it has been observed that transport of some vapors through the membrane can cause swelling of the MFI crystals and can therefore help to close off non-zeolite defects in the membrane (Lee et al. 2008, Yu et al. 2007, Yu et al., 2008). These vapors include n-alkanes, SF₆, i-butane, ethanol, p-xylenes and 2-propanol, which were found to swell MFI crystals by 0.5-1.5 vol% (Lee et al, 2008, Lee et al., 2009, Yu et al., 2007, Sorenson et al. 2009, Sorenson et al., 2008). CD treatment may not be effective in reducing transport of such vapors through defects in the membrane. In an embodiment, none of the components being transported through the membrane in greater than trace amounts produce volume expansion of the molecular sieve crystals in excess of 0.1 vol% or 0.05 vol% at 0.2 MPa feed pressure at 300 K. The volume expansion effect may increase with feed pressure. For example, the volume expansion of SAPO-34 crystals is approximately 0.13 vol% at 1.1 MPa CO₂ feed pressure and 300K (Sorenson, 2010, J. Membr. Sci. ,357, 98-104). In an embodiment, the volume expansion of the molecular sieve crystals is less than 0.5 vol% at 300K over the pressure range of interest.

[0066] Reduction of the amount of flow through intercrystalline defects in the membrane can improve the separation performance of the membrane, especially at pressures of 1 MPa or more. The amount of improvement may depend on the defect density of the membrane. For membrane with relatively high defect

densities (for example an initial CO₂/CH₄ selectivity of less than 125 for a 50/50 (mol%) mixture at 295 K, a permeate pressure of 84 kPa and a feed pressure of 0.2 MPa), cyclodextrin treatment can improve the CO₂/CH₄ separation selectivity of the membrane even for a feed pressure below 1 MPa. The improvement in CO₂/CH₄ selectivities tends to be smaller for membranes with fewer defects at feed pressures less than 1 MPa, but the improvement in the CO₂/CH₄ selectivity can increase with increasing feed pressure.

[0067] Although the description herein contains many specificities, these should not be construed as limiting the scope of the invention but as merely providing illustrations of some of the presently preferred embodiments of the invention. For example, thus the scope of the invention should be determined by the appended claims and their equivalents, rather than by the examples given.

[0068] All references throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

[0069] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art, in some cases as of their filing date, and it is intended that this information can be employed herein, if needed, to exclude (for example, to disclaim) specific embodiments that are in the prior art.

[0070] When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. Every formulation or combination of components described or exemplified can be used to practice the invention, unless otherwise stated. Specific names of compounds are intended to

be exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently. When a compound is described herein such that a particular isomer or enantiomer of the compound is not specified, for example, in a formula or in a chemical name, that description is intended to include each isomers and enantiomer of the compound described individual or in any combination. One of ordinary skill in the art will appreciate that methods, device elements, starting materials, and synthetic methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such methods, device elements, starting materials, and synthetic methods are intended to be included in this invention. Whenever a range is given in the specification, for example, a temperature range, a time range, or a composition range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure.

[0071] As used herein, "comprising" is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. Any recitation herein of the term "comprising", particularly in a description of components of a composition or in a description of elements of a device, is understood to encompass those compositions and methods consisting essentially of and consisting of the recited components or elements. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0072] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and

optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

[0073] In general the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The preceding definitions are provided to clarify their specific use in the context of the invention.

[0074] The invention may be further understood by the following non-limiting examples.

Example 1: Cyclodextrin Treatment of SAPO-34 Membranes

[0075] A simple post-treatment method was developed that increased the CO₂/CH₄ separation selectivity of SAPO-34 membranes. Calcined membranes were soaked in a 1-2% aqueous β-cyclodextrin solution and dried at 473 K. The selectivity for a feed pressure of 0.22 MPa increased 20-150% for membranes with high defect densities, and the percentage of increase was higher as the pressure increased. The selectivities increased less for membranes with fewer defects, but the CO₂/CH₄ selectivity for the best membrane increased by ~17% at 7.1 MPa, from 63 to 74. Carbon dioxide fluxes through these membranes at high pressures only decreased by about 10%, whereas CH₄ fluxes decreased by ~30%. The flux of CF₄, which is too large to enter the SAPO-34 pores and can only permeate through defects, dropped to 20% of its original value at 7.1 MPa, indicating that cyclodextrin effectively blocked permeation through defects. Cyclodextrin may be chemically bonded in the defects. It did not readily dissolve in water at room temperature and it was stable at 473 K; the membrane performance did not change after carrying out separations for 3 days or after long term storage at 473 K.

Experimental methods

Membrane Synthesis and Treatment

[0076] The membrane gel molar ratio was 1.0 Al₂O₃: 1.0 P₂O₅: 0.3 SiO₂: 1.0 TEAOH: 1.6 DPA: 150 H₂O. All chemicals were purchased from Sigma-Aldrich and used as received. In a typical synthesis, the Al source (Al(i-C₃H₇O)₃ (98%) or Al(OH)₃ (50-57% Al₂O₃)), H₃PO₄ (85wt% aqueous solution) and deionized H₂O were stirred for 3 h to form an homogeneous solution, and then Ludox AS-40 colloidal silica (40 wt % SiO₂ suspension in water) was added and the resulting solution was stirred for another 3 h. The tetra-ethyl ammonium hydroxide (35wt% aqueous solution) was added and the solution was stirred for 1 h. After the addition of dipropyl amine (99%), the solution was stirred for 4 days at 318-323 K.

[0077] Most of the membranes were prepared by seeding the inside surface of stainless steel, porous supports (Mott Corporation, 2- μ m pores, 5-cm long) that had non-porous, stainless steel tubes welded onto each end. A membrane was also prepared on an alumina support (Pall Corporation, 5-nm pores). The ends of the alumina supports were glazed with a ceramic glaze at 1170 K (Duncan, Fresno, CA). The SAPO-34 seeds were placed inside the tube and a pipe cleaner was used to distribute the seeds over the inside of the tube. Before seeding, the supports were boiled in DI water for 3 h and dried at 373 K under vacuum for 30 min. The supports, with their outside wrapped with Teflon tape, were then placed in an autoclave, which was filled with synthesis gel. Hydrothermal synthesis was carried out at 493 K for 4-6 h, and the membranes were then washed with DI water and dried for ~2 h at 340 K. The membranes were calcined in air at 670 K for 4 h to remove the templates. The calcination heating and cooling rates were 0.7 and 0.9 K/min, respectively.

[0078] The seed gel molar ratio was 1.0 Al₂O₃ : 1.0 P₂O₅ : 0.3 SiO₂ : 1.0 TEAOH : 0.8 DPA: 0.8 CHA: 52 H₂O. In a typical synthesis, Al(i-C₃H₇O)₃ (98%), H₃PO₄ (85wt% aqueous solution), and deionized H₂O were stirred for 3 h to form an homogeneous solution, and then Ludox AS-40 colloidal silica (40 wt % SiO₂ suspension in water) was added and the resulting solution was stirred for another 3 h. The templates, tetra-ethyl ammonium hydroxide (35 wt% aqueous solution), dipropylamine (99%) and cyclohexylamine (99%) were then added, and the solution stirred for 4 days at 318-323 K. The solution was then placed in an autoclave and held at 493 K for 24 h. After the solution was cooled to room temperature, it was

centrifuged at 100 Hz (6000 rpm) for 10 min to separate the seeds, which were then washed with DI water. This procedure was repeated three times. The resulting precipitate was dried overnight and calcined at 823 K for 8 h. The calcination heating and cooling rates were both 1.0 K/min, respectively.

[0079] Calcined SAPO-34 membranes were soaked in 0.5-5 wt% aqueous solutions of α or β -cyclodextrin at room temperature (RT) for 5 min to 4 h and then dried at RT for 4 h. The membranes were stored at 473 K overnight before permeation and separation experiment.

Permeation and separations measurements

[0080] Carbon dioxide/methane mixtures (50/50 mol%) were separated at 295 K in a flow system with feed pressures from 0.22 to 7.1 MPa. Feed flows were controlled by mass flow controllers and ranged from 250 cm³/min (standard conditions) at low pressure to 1500 cm³/min at high pressure. The permeate pressure was fixed at 84 kPa, and no sweep gas was used. Permeate and retentate fluxes were measured with bubble flow meters, and compositions were analyzed by a GC (SRI 8610C) with a Hayesep D column at 373 K and a TC detector. An automated sample loop took samples from the feed and permeate streams. The tubular membranes were sealed in a stainless steel module with silicone O-rings. The leak integrity of the module was verified by replacing the membrane with a solid stainless steel tube. The leak rate for an 8 MPa pressure drop across the O-ring was < 0.2 % of the measured CH₄ flux for a 50/50 CO₂/CH₄ mixture at the same pressure drop. Concentration polarization was minimized by using a Teflon spacer to reduce the cross section for feed flow and increase gas velocity [13], and a high pressure gas booster to obtain a feed pressure up to 7 MPa at high velocity. Carbon tetrafluoride fluxes were measured in dead end module at 295 K and for feed pressures from 0.9 to 5.8 MPa. The CO₂/CH₄ separation selectivity α was defined as:

$$\alpha = \frac{J_{CO_2} / \Delta p_{\log\text{-mean}, CO_2}}{J_{CH_4} / \Delta p_{\log\text{-mean}, CH_4}}$$

where J (mol/m² s) is the steady-state flux of CO₂ or CH₄ and $\Delta p_{\log\text{-mean}}$ is the log-mean partial pressure drop.

Permporometry

[0081] Permporometry measurements were carried out in a flow system similar to that described previously (Cao et al., 1993, J. Membr. Sci. 38, 221). The feed was mostly helium, with 3% i-butane and various concentrations of benzene, and the permeate was helium with benzene at the same concentration as in the feed. Both feed and permeate were at 82 kPa so that capillary condensation was maximized, since even small pressure drops suppress liquid buildup in the defects (Tokay et al., 2009, J. Membr. Sci., 224, 259). The flux of i-butane was measured as a function of benzene concentration. Since i-butane (0.5 nm kinetic diameter) is significantly larger than the SAPO-34 pores (0.38 nm) it only permeates through the defects. Benzene was added to both feed and permeate by flowing each of these streams through two liquid bubblers in series. As the benzene concentration in the feed and permeate increased, benzene capillary condensation closed off i-butane flux through defects with increasingly larger pores sized. The corresponding pore radii were calculated using the Kelvin equation and assuming that i-butane transport was by Knudsen diffusion. The percentage change of the i-butane flux at a given range of pore radii is a measure of the defect area in this size range. The defect areas were calculated for slit-shaped defects using the methods described by Wang et al. (2009, J. Membr. Sci. 300, 259) and Cao et al. (1993, J. Membr. Sci. 38, 221)

Results and Discussion

Low Pressure Separations

[0082] Table 2 shows the CO₂ permeances and CO₂/CH₄ selectivities, at a feed pressure of about 0.2 MPa, for a SAPO-34 membrane that was exposed to β -cyclodextrin solutions at different conditions. The CO₂/CH₄ selectivity for membrane M1 increased from 110 to 190 with only a 15% decrease in CO₂ permeance after exposure to a 1% CD solution. The CO₂/CH₄ selectivity increased further to 240 and 270, after two additional treatments with 1.8% β -cyclodextrin solution, and the CO₂ permeance decreased overall by about 32%. The selectivity and permeance did not change with the membrane dried for additional 3 days at 473 K (default drying: overnight at 473 K). Thus, cyclodextrin is thermally stable to at least at 473 K in the defects; β -CD melts/decomposes at 563 K. The selectivity only changed slightly

when the membrane was soaked in DI water for 4 h, indicating cyclodextrin that was adsorbed in the defects dissolved slowly.

Table 2. The effect of CD treatment on SAPO-34 membranes for CO₂/CH₄ separation at 295 K and feed pressure of 0.22 MPa.

Membrane	Treatment	CO ₂ permeance ×10 ⁷ [mol/(m ² ·s·Pa)]	% original permeance	CO ₂ /CH ₄ selectivity	% selectivity increase
M1	untreated	4.7	----	110	---
	1% β-CD, 4 h	4.0	85%	190	73%
	1.8% β-CD, 4 h	3.4	72%	240	118%
	1.8% β-CD, 4 h	3.2	68%	272	147%
	473 K for 3 d	3.3	70%	268	144%
M1A	Re-calcined	4.8	----	110	----
	1.8% β-CD, 5 min	3.7	77%	230	109%
	473 K for 2 d	4.0	83%	211	92%
	473 K for 4 d	4.1	85%	223	103%
M1B	Re-calcined	4.7	----	110	----
	1.8% β-CD, 30 min	4.7	100%	128	16%
	1.8% β-CD, 30 min	4.3	92%	190	73%

[0083] The initial permeance and selectivity of membrane M1 was recovered after the membrane was calcined at 673 K for 4h (membrane M1A). The CO₂/CH₄ selectivity then increased to 230 when the membrane was soaked in 1.8% β-cyclodextrin solution for 5 min, and the CO₂ permeance dropped 27%. The CO₂/CH₄ selectivity did not change after 4 days at 473 K, but the CO₂ permeance increased 10%. After the membrane was calcined again (membrane M1B), the original permeance and selectivity were obtained. Two exposures for 30 min each to a 1% β-CD solution, followed by drying at 473 K, yielded a membrane with a CO₂/CH₄ selectivity of 190 and only a 8% loss of permeance.

[0084] Table 3 shows CO₂ permeances and separation selectivities for four membranes that initially had a range of CO₂/CH₄ separation selectivities. They were treated with α-CD and β-CD solutions at different conditions. The α-CD molecule has a smaller outside diameter and cavity but is more soluble in water than β-CD

(Table 1). The CO₂/CH₄ separation selectivity of membrane M2 increased from 152 to 199, after one treatment with a 5% α-CD solution. The CO₂ permeance decreased by 60%, which is a much larger drop than observed for membranes exposed to β-CD solutions. The CO₂/CH₄ selectivity for membrane M3, which was treated with 2% α-CD solution instead of 5%, increased by 33%, and the CO₂ permeance was essentially unchanged. Excess CD apparently blocks permeation through SAPO-34 pores.

[0085] Similar results were obtained with membranes M4 and M5, which had higher initial CO₂/CH₄ selectivities. The CO₂/CH₄ selectivities increased from 197 to 252 and 211 to 283, respectively. The CO₂ permeances of membranes M4 and M5 were only ~15% lower than the original values after drying at 493 K for 2 d. Treatment with 1-2% CD solutions increased the CO₂/CH₄ selectivity at 0.22 MPa feed pressure without losing much permeance. Exposure times from 5 min to 4 h gave similar results.

Table 3. The effect of CD treatment of SAPO-34 membranes on CO₂/CH₄ separation at 295 K and feed pressure of 0.22 MPa

Membrane	Treatment	CO ₂ permeance ×10 ⁷ (mol/(m ² ·s·Pa))	% original permeance	CO ₂ /CH ₄ Selectivity	% selectivity increase
M2	untreated	3.6	----	152	----
	5% α-CD, 4 h	1.5	42%	199	31%
M3	untreated	2.3	----	150	----
	2%α-CD, 5 min	2.2	96%	200	33%
	473 K for 2 d	2.3	100%	195	30%
M4	untreated	5.6	----	197	----
	1% β-CD, 30 min	5.1	91%	252	28%
	473 K for 2 d	5.2	93%	239	21%
M5	untreated	3.6	----	211	----
	1% β –CD, 5 min	2.4	67%	283	34%
	473 K for 2 d	3.1	86%	270	28%

High Pressure Separations

[0086] Four SAPO-34 membranes (M6-M9) that had low-pressure CO₂/CH₄ selectivities above 200 were used for CO₂/CH₄ separations at feed pressures up to 7.1 MPa before and after treatment with a 1.8% β -CD solution and holding at 473 K overnight. The CO₂/CH₄ selectivities of all membranes increased at higher pressure after the CD treatment. As shown in Fig. 1a, the selectivity for membrane M6 increased more at higher pressure. At 0.14 MPa pressure drop, the selectivity increased by 9% from 270 to 295, whereas at 4.6 MPa, it increased by 36%, from 49 to 67. Below 1 MPa, CO₂ and CH₄ fluxes were similar before and after treatment (Fig. 1b), but at 4.6 MPa, the percentage decrease in CH₄ flux (35%) was more than three times the percentage decrease in CO₂ flux (10%) after the CD treatment.

[0087] As pressure increases, the flux through SAPO-34 pores increases less than linearly with pressure because the loading increases less than linearly at high pressure (Langmuir isotherm behavior). In contrast, the flux through defects increases linearly (Knudsen flux) or more than linearly (viscous flux), depending on the defect sizes, so that a larger fraction of the total flux is through defects at higher pressures. As shown in Fig. 1b, the CO₂ flux increased less than linearly with pressure, but the CH₄ flux increased more than linearly before CD treatment, and thus the CH₄ permeance increased as the pressure increased and the selectivity decreased. After CD treatment, the CH₄ permeance decreased with pressure. This behavior suggests that many of the defects that had viscous flow through them were blocked by the CD treatment. Thus defects that were not selective for CO₂/CH₄ separations were preferentially blocked by CD adsorption.

[0088] Similar results were obtained for membrane M7, with separation properties close to that of membrane M6, as shown in Fig. 2a and 2b. The CO₂/CH₄ selectivity increased by about 15% at 0.14 MPa but it increased by 30% at 4.6 MPa (Fig. 2a). The CH₄ permeance decreased more with pressure after CD treatment, which indicated a decreased contribution of viscous flow. The CO₂ flux decreased by 10 % at 4.6 MPa, whereas the CH₄ flux decreased 33% (Fig. 2b), which led to 30% increase in selectivity. A third membrane (M8) showed similar behavior with a 17% increase in CO₂/CH₄ selectivity (from 63 to 74 at 7.2 MPa) but only small increases (~5%) at low pressures. Membrane M9, with an initial low pressure selectivity of

220. showed similar selectivity increases over the whole pressure range (Figure 3). The CO₂/CH₄ selectivity increased 15% at a pressure drop of 5.7 MPa and 20% at lower pressures (increase of 15-20% over the whole pressure range). The CH₄ and CO₂ fluxes decreased 23% and 15% respectively at 5.7 MPa (Figure 4).

High defect density membranes at high pressure

[0089] Two membranes with high defect density were also post-treated with cyclodextrin (4 h contact time) and evaluated at high pressure up to 4.7 MPa.

[0090] Both treated membranes increased the selectivity, and the relative increase was larger as the pressure increased. For instance, membrane Mott-D14 (also referred to as M10) originally had a selectivity value of 23 at 4.7 MPa that changed to 44 after the treatment (Table 4). This is a 91% increase (see Figure 5a). The CH₄ binary permeance decreased more than 50%. However, at low pressure (0.14 MPa), even though the selectivity increased significantly, from 180 to 239, the improvement was relatively lower than at high pressure. Note that the binary CH₄ permeance originally increasing with pressure was almost constant after treatment. Analogous results were observed for membrane Mott-D13 (Table 5).

[0091] These membranes showed higher relative increase of selectivity at high pressure in comparison to the less defective membranes. Mott-D14 and Mott-D13 with original selectivities values of 23 and 28 increased the selectivity 91% and 64% respectively at 4.7 MPa after treatment. Thus, the percentages of increase in selectivity were higher in comparison to 35 % and 12% increases of M6 and M8 with original selectivities of 49 and 63 at the same pressure. The relatively higher increase in the selectivity observed for the high defect density membranes showed that cyclodextrin molecules are blocking defects significant in size and more CD molecules can be adsorbed into the larger defects of these membranes. Consequently, a higher fraction of defect area in relation to the membrane area is able to be repaired by the CD treatment in the case of the high defect density membranes.

Table 4. Mott-D14 (before / after CD treatment 4h)						
Pressure	Permeance				Select	
MPa	mol/m ² s Pa x 10 ⁹		% orig. value			% increase
	CO2	CH4	CO2	CH4		
0.14	280 / 240	1.5 / 1.0	86	67	180 / 239	33
1.4	130 / 100	2.1 / 1.0	77	48	61 / 105	72
2.8	80 / 69	2.2 / 1.0	86	45	36 / 66	83
4.6	57 / 47	2.4 / 1.1	83	46	23 / 44	91

Table 5. Mott-D13 (before / after 4h CD treatment)						
Pressure	Permeance				Select	
MPa	mol/m ² s Pa x 10 ⁹		% orig. value			% increase
	CO2	CH4	CO2	CH4		
0.14	460 / 410	2.1 / 1.6	89	76	214 / 254	19
1.4	200 / 180	3.0 / 1.7	90	57	67 / 101	51
2.8	120 / 110	3.2 / 1.8	92	56	39 / 65	67
4.6	90 / 79	3.3 / 1.7	88	52	28 / 46	64

The largest improvements in selectivity were obtained with a membrane (M11) grown on an alumina support that had a selectivity of 154 at 0.22 MPa (before CD treatment). The low pressure selectivity increased to 239 after the beta-CD treatment, and at 4.6 MPa the selectivity increased a factor of 2.5 (from 15 to 38) with only 22% loss in CO₂ flux. The CH₄ flux decreased to about 1/3 of its original value at 4.6 MPa. Figure 6a shows the selectivity as a function of feed pressure while Figure 6b shows the flux as a function of feed pressure.

Carbon tetrafluoride permeation

[0092] Carbon tetrafluoride (CF_4) has a kinetic diameter of 0.47 nm and thus it does not permeate through the SAPO-34 pores and only permeates through defects larger than 0.47 nm. The CF_4 flux increased more than linearly with pressure for membrane M9 before CD treatment (Fig. 7a) so that the permeance increased with pressure (Fig. 5b). The CD treatment decreased the CF_4 flux over the entire pressure range (to 20% of its original value at 5.7 MPa), as shown in Fig. 7a, and the permeance decreased as the pressure increased (Fig. 7b). This pressure dependence suggests that many of the defects that contributed to viscous flow were blocked.

[0093] Figures 7a and 7b show that at a given pressure, the CH_4 binary flux decreased more than the CF_4 flux following CD treatment. The pressure drop for CH_4 is the log mean pressure drop in the mixture. The CH_4 flux is a combination of flow through SAPO-34 pores and through defects (Knudsen and viscous). The CH_4/CF_4 Knudsen selectivity is 2.3 and thus, CD molecules inside the defects are able to drop more CH_4 than CF_4 flux at the same pressure, as long as Knudsen contribution through the defects is not negligible.

Permporometry

[0094] Permporometry measurements were carried out with membrane M9 before and after CD deposition. The i-butane performance, plotted vs. the defect diameter (which is related to the benzene activity in Figure 8, indicates that both the overall defect area and the defect sized decreased after CD deposition. About 37% of the i-butane permeance in the absence of benzene was blocked by CD. About half of the i-butane flux was through defects smaller than about 8 nm for the original membrane (Fig. 8) and about 40% of the flux remained after all defects smaller than about 30 nm were blocked by benzene (corresponding to the highest benzene activity measured). The defect areas were calculated for slit-shaped pores using the method described by Wang et al. (2009, J. Membr. Sci. 300, 259). The defects smaller than 8 nm in the original membrane accounted for about 91% of the total defect area. After CD deposition, approximately 80% of the i-butane flux was through defects that were smaller than 2 nm and their area was about 99% of the

total defect area. The remaining 20% of the flux was through defects that were 15-20 nm in size with an area of only about 1% of the total defect area. No defects (within detection limits) were larger than 20 nm. Note that these defect sizes are upper limit estimates because permeation through defects is limited by the narrowest opening in an irregular shaped defect, but condensation requires the opening to be long enough to stabilize a liquid layer. For example, a 20nm defect that is only 1 nm long (a pinch point) is not expected to form a stable liquid layer. Instead, condensation would only occur in a wider and longer part of the membrane at a benzene activity higher than that required for condensation in a 2-nm defect.

Conclusions

[0095] Exposing SAPO-34 membranes to dilute aqueous solutions of cyclodextrin, followed by drying at 473 K, increased their CO₂/CH₄ separation selectivities while only decreasing their CO₂ permeances by 10-20%. The modified membranes were not changed by water leaching or storage at 473 K, but the original permeation properties were obtained by calcination at 673 K. The low pressure selectivity increased significantly for membranes with many defects, but the increases were smaller for membranes with higher selectivities. The largest increases in selectivity for a membrane with few defects were about 30% at 4.6 to 5.7 MPa with a ~10% loss in CO₂ permeance, but up to 90% increase in selectivity was obtained with high defect density membranes. Cyclodextrin decreased the flux of CF₄, which can only permeate through defects larger than 0.47 nm, by 75 % at 4.6 MPa, and the CF₄ permeance, which increased with pressure before CD treatment, was mostly constant after treatment, indicating less viscous flow.

Example 2: Temperature-Programmed Oxidation of Cyclodextrin-Treated SAPO-34 Membranes

[0096] Temperature-programmed oxidization (TPO) was carried out in a system similar to that described previously [18]. The calcined SAPO-34 membranes were prepared as described in Example 1 then soaked in 1.8 wt % β-CD aqueous solution for 4 h and dried at RT for 4 h and then at 473 K overnight. The membranes selected for treatment had a relatively high defect density. The SAPO-34 membrane was placed in a quartz tube. The quartz reactor was surrounded by

an electrical furnace consisting of Kanthal wire wrapped around a quartz cylinder, and a thermocouple was placed in the center of the membrane. A temperature controller was used to control the heating rate at 10 K/min. The flow rate of oxygen was 25 cm³/min. The highest temperature used was 1073 K. The reactor was purged with helium at a flow rate of 50 cm³/min at 373 K for 30 min before ramping the temperature. The mass signals were monitored immediately downstream of the reactor using a Blazer QMA 125 quadrupole mass spectrometer.

[0097] Figure 9 illustrates a plot of H₂O and CO₂ pressure as a function of temperature during the TPA process. The CO₂ peak was used to calculate the amount of β-cyclodextrin in the membrane. Two SAPO-34 membranes were tested; they had 5 mg and 18 mg of beta-cyclodextrin in the membrane respectively. The surface area of the stainless steel support was about 7 cm². The amount of beta-CD per mm² referenced to this surface area was 0.0071 mg/mm² and 0.025 mg/mm², respectively. Using a molecular weight of 1135 for β-CD, the estimated average amount of β -CD per unit area is approximately 6.3 x 10⁻⁹ moles/mm² and 2.2 x 10⁻⁸ moles/mm².

[0098] The thickness of SAPO-34 layer was approximately 5-6 micrometers. For a thickness of 5.5 micrometers, the nominal volume of the SAPO-34 membrane approximately 3.9 mm³. Therefore, the estimated average amount of β -CD per unit volume of SPO-34 membrane is approximately 1.3 mg/mm³ and 4.6 mg/mm³. Using a molecular weight of 1135 for β-CD, the estimated average amount of β -CD per unit volume of SPO-34 membrane is approximately 1.1 x 10⁻⁶ moles/mm³ and 4.1 x 10⁻⁶ moles/mm³.

Example 3: Cyclodextrin Treatment of B-ZSM-5 Membranes

[0099] Three B-ZSM-5 membranes (A,B, C) were synthesized by secondary growth on the inner surface of tubular α-alumina supports (0.2 mm pores, Inopor). The supports were first boiled in DI water for 3 h, then soaked in anhydrous ethanol for 3 h, and then dried. Silicalite-1 crystals were used to seed the inside of the support surface, and they were made from a gel with a molar composition of 9 TPAOH:24 SiO₂:500 H₂O :96 EtOH, where tetrapropylammonium hydroxide (TPAOH, 1.0 M aqueous solution, Aldrich) was used as the template and

tetraethoxysilane (TEOS, 98% Aldrich) was used as the silicon source. The silicalite-1 seeds were synthesized at 358 K for 3 days. The α -alumina supports were dip-coated with a suspension of silicalite-1 seeds (1 wt% seeds in ethanol). The secondary growth gel had a molar composition of 16 TPAOH : 80 SiO₂ : 6.5 H₃BO₃ : 5000 H₂O : 320 EtOH; this composition has a Si/B ratio of 12.5. The gel was aged for 1 day. The outside of the supports were wrapped with Teflon tape, and then placed in an autoclave, which was then filled with synthesis gel. The support was soaked in the gel at room temperature from 0 to 14 h before hydrothermal synthesis was carried out at 458 K for 4 h. The membranes were then washed with DI water, dried for approximately 2 h at 383 K, and calcined in air at 673 K for 4 h to remove the templates. The calcination heating and cooling rates were 0.7 and 0.9 K/min, respectively.

[00100] β -cyclodextrin (CD) was deposited in the MFI membranes from a saturated aqueous solution (1.8 wt% CD) at 295 K. One end of the support was sealed and its interior was filled with the CD solution. The open end of the support, which was held vertical, was then gradually pressurized with air to 0.7 MPa and held at that pressure for 1-2 h. The pressure was then slowly released, the membrane was dried overnight at 423 K, and then stored under vacuum (<0.1 kPa) at 453 K. Thermogravimetric analysis of CD shows it does not decompose until approximately 500 K (Shen et al, 2005, Spectrochim. Acta Part A: Mol. Biomol. Spectros. 61, 1025-1028). In attempts to remove CD from some membranes, they were calcined in air and in oxygen at 673 K for 4 h.

[00101] Single-gas fluxes of He, H₂, n-butane, i-butane, and SF₆ was measured at 295 K in a dead end mode system described previously (Poshusta et al. 1999, J. Membr. Sci., 160, 115-125) using a stainless steel module with o-ring seals. The feed pressure was 110-130 KPa and the permeate pressure was approximately 84 kPa. (ambient pressure in Boulder, CO). Permeate fluxes were measured with a bubble flow meter. Before each measurement, the system was flushed with the test gas. Membranes were calcined or heated under vacuum to 453 K for at least 12 h following measurement with a gas (n-butane, i-butane, SF₅) that swelled the MFI crystals. Prior to single-gas measurements, the He permeances were measured

and were within 5% of their previous values, indicating that the membranes had not changed significantly during storage or calcination.

[00102] Permporometry, also known as adsorption branch permporosimetry (Hedlund et al, 2003, J. Membr. Sci. 222, 163-179; Hedlund et al., 2002, Micropor. Mesopor. Mater. 52, 179-189) was used to determine the fraction of flow through defects at room temperature by measuring the helium flux as a function of the activity of a vapor in the feed. The membranes were sealed in a stainless steel module with Viton o-rings. At low activities, adsorption blocks the helium flux through MFI pores, so that the remaining helium flux is through defects. Permporometry experiments were performed using benzene (>99.9%; Signal-Aldrich) or n-hexane (99%, Fluka). Their activities were adjusted by saturating a helium stream with the hydrocarbon using two temperature-controlled liquid bubblers in series and then mixing the saturated stream with a pure helium stream. The hydrocarbon activities were controlled by adjusting the ratio of the two helium streams with mass flow controllers and adjusting the temperature of the bubblers.

[00103] Prior to permporometry measurements, the membranes were calcined in air at 673 K if they did not contain CD. If they contained CD, they were stored under vacuum (<1 kPa) at 453 K for at least 12 h. The helium feed flow rate was 200 sccm, and a back pressure regulator controlled the feed pressure at 110 kPa. The permeate side was kept at 84 kPa, and a mass flow meter and a bubble flow meter were used to measure the helium flow rate. A pressure drop across the membrane minimized capillary condensation in the defects; capillary condensation was only seen in this type MFI membrane for pressure drops less than 20 kPa (Tokay, 2009). Additionally, the He pressure drop was kept constant to maintain a constant He driving force. An activated-carbon and a molecular sieve (MS 13X Dunniway) trap on the permeate line removed the adsorbate molecules from the helium stream before the permeate flow measurements. Prior to each permporometry experiment, the He permeances were measured and they were within 5% of their previous values, indicating that the membranes had not changed significantly during storage or calcination.

Temperature Programmed Oxidation

[00104] A membrane with CD deposited in it (membrane C) was placed into a quartz reactor which was located in a resistively heated furnace. Air (zero grade, Airgas) flowed through the reactor at 25 sccm, and its rate was controlled with a mass flow controller. The membrane temperature was measured by a thermocouple inserted into the center of the membrane support. The temperature was ramped at 10K/min from 295 to 870 K, and effluent gas from the reactor was analyzed with a quadrupole mass spectrometer (SRI) that was interfaced to a computer.

Permporometry results

[00105] During permporometry on membrane A at room temperature, 63% of the helium flow remained after benzene adsorption, indicating that 63% of the original helium flux was through defects, because benzene does not have a significant effect on the size of MFI crystals. CD decreased the helium flux for membrane A. However, the fraction of helium flow through defects was still 65%. Since the helium flux was lower with CD in the defects, but the fraction of flow through defects did not decrease, CD apparently deposited in defects that were in series with zeolite pore pathways and thus blocked some flow through MFI pores. Benzene permporometry of membrane B indicated that 52% of the helium flux at room temperature was through defects. After CD deposition, only 30% of the helium flow was through defects, indicating that CD preferentially blocked flow through defects.

[00106] In contrast, for an n-hexane activity of 0.005, the helium flux dropped more than three orders of magnitude; only 0.05% of the helium flow remained. This type of behavior has been reported previously for MFI membranes (Lee et al, 2008, J. Membr. Sci. 321, 3090-315; Yu et al., 2007, J. Membr. Sci. 298, 182-189; Yu et al., 2008, Ind. Eng. Chem. Res. 47, 3943) and arises because n-hexane swells MFI crystals and almost closes off defects. XRD measurements showed that MFI crystals expand about 1.15 vol% at saturation n-hexane loading, whereas benzene does not expand MFI crystals significantly (Sorenson et al., 2009, Ind. Eng. Chem. Res., 47, 9611-9619; Sorenson et al. 2008, Ind. Eng. Chem. Res. 47, 9611-9616).

The normalized helium flux when n-hexane adsorbed in membrane A after CD deposition was 20%, which is more than two orders of magnitude higher than for the original membrane. This higher flux is attributed to inhibition of adsorbate induced swelling of MFI crystals by CD in the defects. Without wishing to be bound by any particular belief, the CD is believed to act like a molecular shim in the defects. That is, the defects did not shrink much when n-hexane adsorbed, and the helium flow, which was mostly through defects, was higher than without CD in the membrane. For membrane B, when n-hexane adsorbed, only 0.31% of the helium flow remained. Apparently defects were slightly larger in membrane B than membrane A, so that crystal swelling did not close them off as effectively. After CD deposition, after n-hexane adsorbed, the fraction of helium flux through defects was more than an order of magnitude higher than through the original membrane (7.5% vs. 0.31%). As observed for membrane A, n-hexane swelled the crystals enough to decrease the flux through defects, but it decreased the flux much less than before CD deposition.

Temperature-programmed oxidation Results

[00107] Only H₂O and CO₂ were detected in significant quantities during TPO of membrane C. They each formed in two peaks at 600 and 760 K. A third water peak at 375 K was probably adsorbed H₂O. The overall H/C ratio was 2, which is the same as the ratio in CD, but the ratio was 4 for the low-temperature peak, and 0.5 for the high-temperature peak. That is, oxidation appeared to preferentially dehydrogenate the CD at lower temperatures, and the carbon –rich species that remained was oxidized at higher temperature. Much of the CD decompose/oxidized above 673 K during TPO, so that these reactions may not be complete during calcination at 673 K for 4 h. Instead, calcination at 673 K may produce some carbon-rich decomposition products that remain in the defects and inhibit MFI crystal swelling. The TPO result indicates that CD probably did not decompose/oxidize when membranes containing CD were stored at 453 K in air.

[00108] In addition to CO₂ and H₂O formation, an organic residue deposited on the wall of the reactor at the furnace outlet. Thus the amount of CD in the membrane estimated from CO₂ formation during TPO is a lower limit. The reactor was weighted before and after removing the organic residue, which was assumed to

be glucose for estimating the number of moles. The amount of CD deposited in the membrane was estimated to be 20 +/-10 mg, which corresponds to 2.8 +/- 1.5 mg/cm². The temperatures at which the CO₂ and H₂O peaks formed are similar to those reported for TGA measurements for CD alone (Shen, 2005), indicating that the MFI zeolite did not significantly catalyze CD decomposition or oxidation.

[00109] References

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CLAIMS

We claim:

1. A method of treating a calcined crystalline molecular sieve membrane comprising zeolite pores and non-zeolite pores, the method comprising the steps of:

- a. preparing a treatment solution comprising cyclodextrin molecules and a solvent;
- b. contacting the membrane with the treatment solution; and
- c. removing solvent from the membrane;

wherein the outside diameter of the cyclodextrin molecules is larger than the characteristic zeolite pore size.

2. The method of claim 1, wherein the characteristic zeolite pore size is from 0.3 to 0.8 nm.
3. The method of claim 1, wherein the membrane is selected from the group consisting of SAPO-34, AIPO-18, DDR, zeolite A, ZSM-5, silicalite-1, and TS-1.
4. The method of claim 3, wherein the membrane is a SAPO-34 membrane.
5. The method of any of claims 1-4, wherein the treatment solution solvent is water and the cyclodextrin concentration is from 0.5-5 wt%.
6. The method of claim 5, wherein the cyclodextrin concentration is from 1 to 2%.
7. The method of any of claims 1-4, wherein the cyclodextrin molecules are α -CD, β -CD, γ -CD or a combination thereof.
8. The method of any of claims 1-4, wherein the membrane is contacted with the treatment solution for a time from 5 minutes to 4 hours.

9. The method of any of claims 1-4, wherein solvent is water and solvent is removed from the membrane by heating the membrane to a temperature above the boiling point of water and below the decomposition temperature of the cyclodextrin molecules.
10. The method of claim 9, wherein the membrane is heated to a temperature of at least 200 °C.
11. A method for separating molecules of a first substance from molecules of a second substance, the method comprising the steps of:
 - a. providing a crystalline molecular sieve membrane, the membrane comprising zeolite pores and non-zeolite pores and having a feed side and a permeate side wherein a sufficient quantity of cyclodextrin molecules is adsorbed within the non-zeolite pores of the membrane to improve the selectivity of the membrane to the first substance over the second substance;
 - b. providing a feed stream including molecules of the first and second substances at the feed side of the membrane;
 - c. providing a driving force sufficient for permeation of molecules of the first substance through the membrane, thereby producing a permeate stream enriched in molecules of the first substance.

wherein the outside diameter of the cyclodextrin molecules is larger than the characteristic zeolite pore size.

12. The method of claim 11, wherein the membrane is selected from the group consisting of SAPO-34, AIPO-18, DDR, zeolite A, ZSM-5, silicalite-1, and TS-1.
13. The method of claim 12, wherein the membrane is a SAPO-34 membrane.
14. The method of any of claims 11-13, wherein the cyclodextrin molecules are α -CD, β -CD, γ -CD or a combination thereof.

15. The method of any of claims 11-13, wherein the amount of cyclodextrin (CD) per unit volume of molecular sieve membrane is greater than 1×10^{-7} moles/mm³.
16. The method of any of claims 11-13, wherein the first substance is CO₂ and the second substance is CH₄.
17. A cyclodextrin-treated polycrystalline molecular sieve membrane comprising
 - a. a molecular sieve membrane having zeolite pores with a characteristic size less than 1.0 nm and non-zeolite pores; and
 - b. cyclodextrin molecules adsorbed within the non-zeolite pores of the membranewherein the amount of cyclodextrin per unit volume of molecular sieve membrane is greater than 1×10^{-7} moles/mm³.
18. The membrane of claim 17, wherein the molecular sieve membrane is selected from the group consisting of SAPO-34, AIPO-18, DDR, zeolite A, ZSM-5, silicalite-1, and TS-1.
19. The membrane of claim 18, wherein the molecular sieve membrane is a SAPO-34 membrane.
20. The membrane of any of claims 17-19, wherein the cyclodextrin molecules are α -CD, β -CD, γ -CD or a combination thereof.

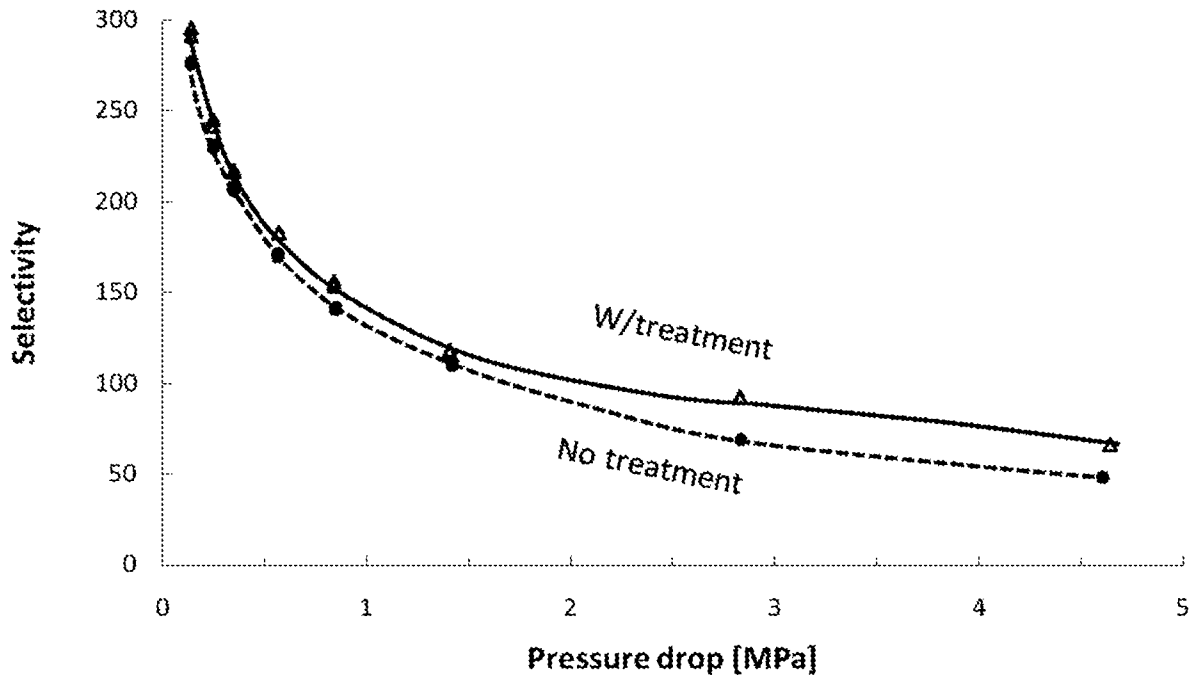


Figure 1a.

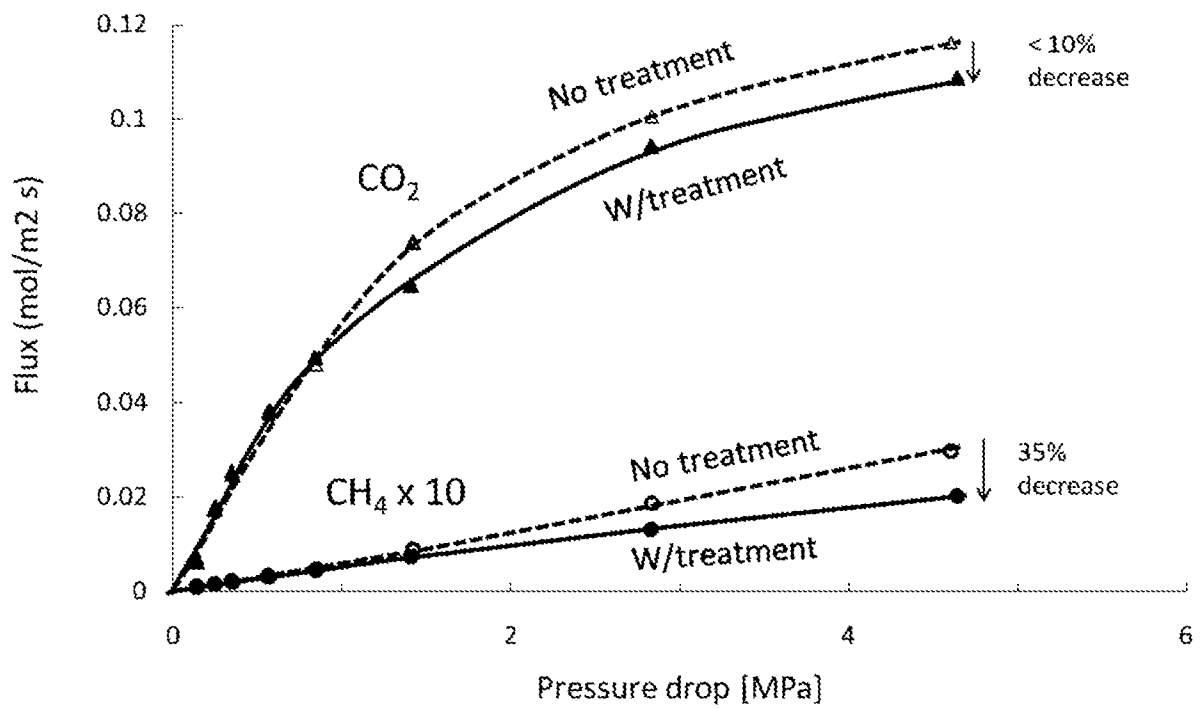


Figure 1b

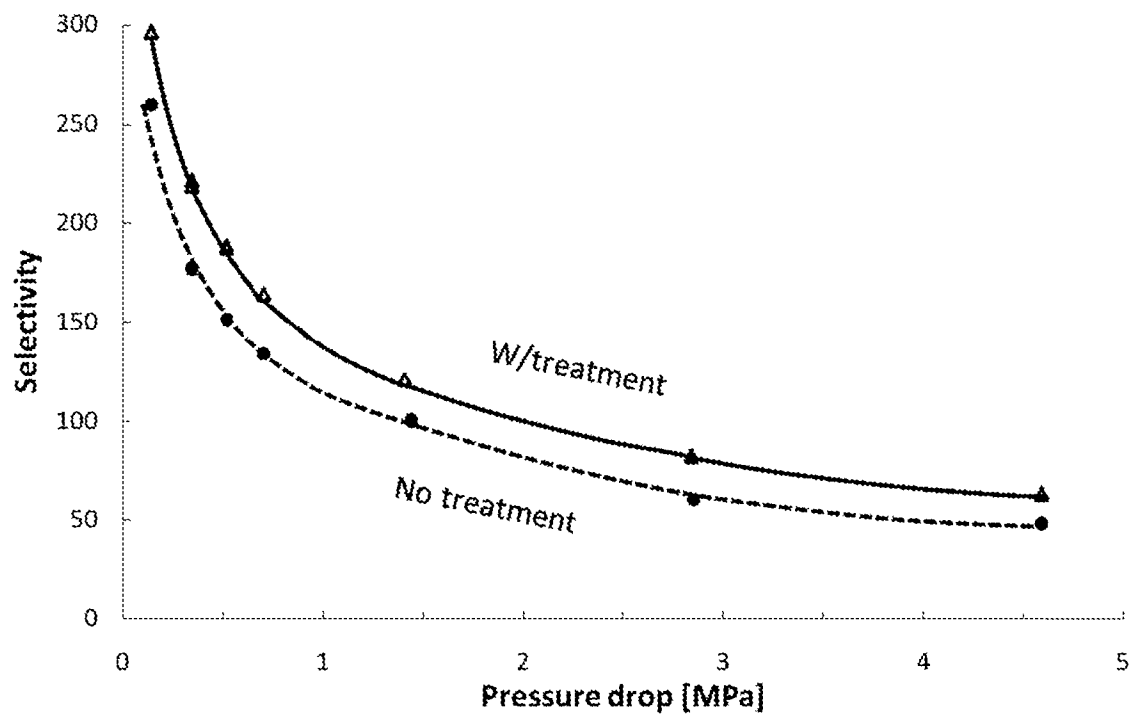


Figure 2a

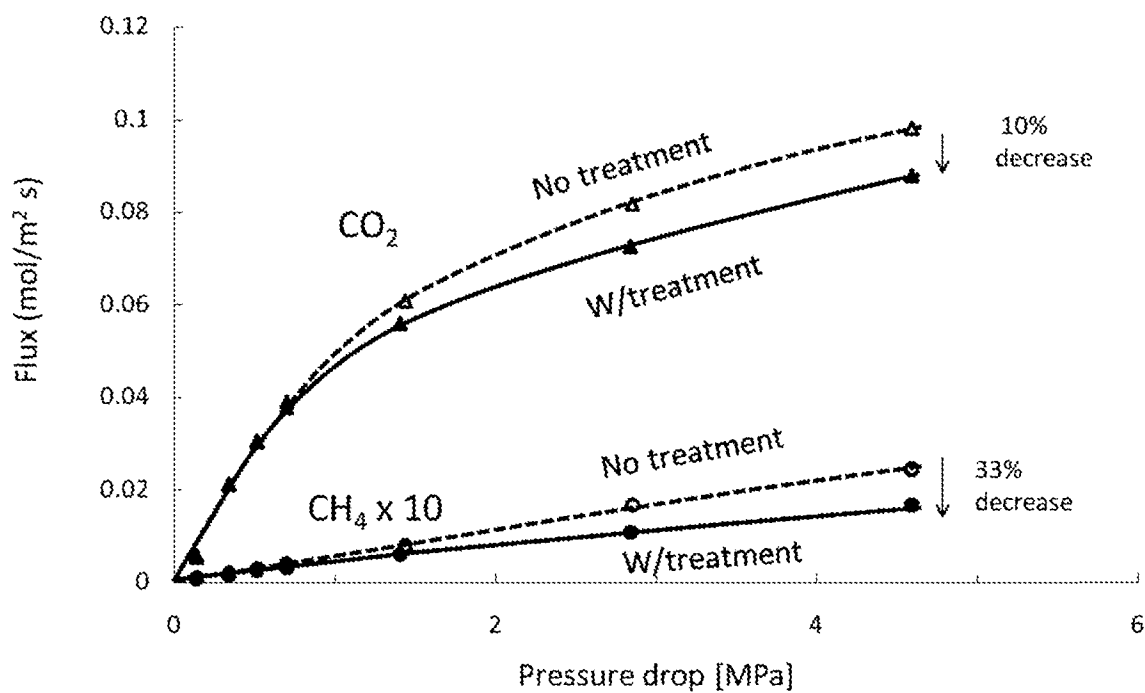


Figure 2b

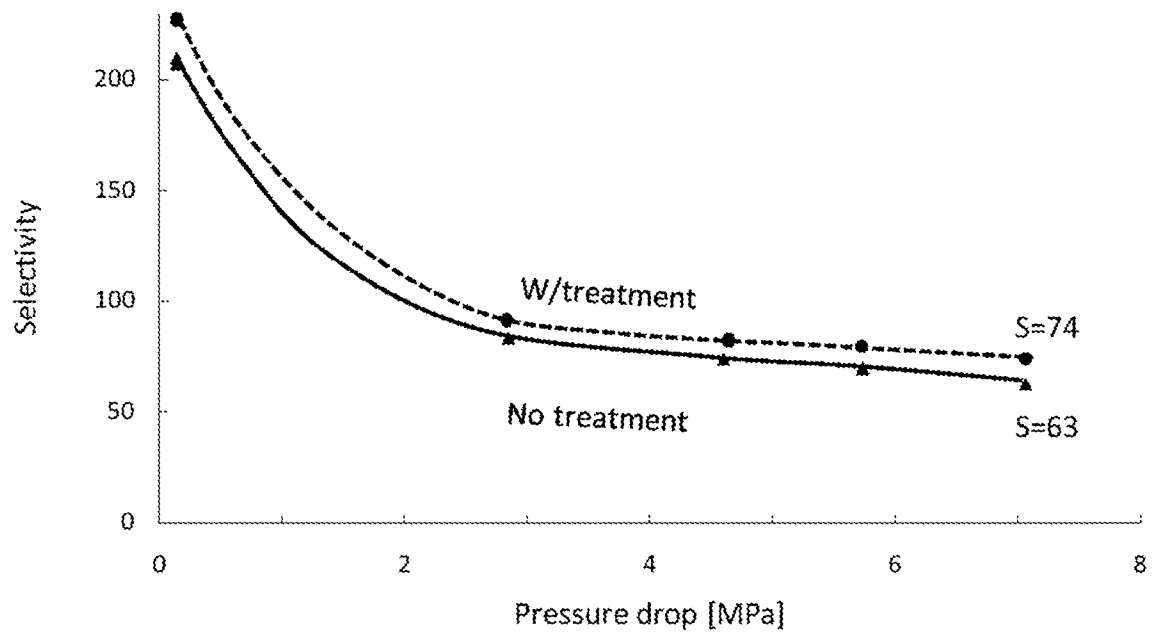


Figure 3

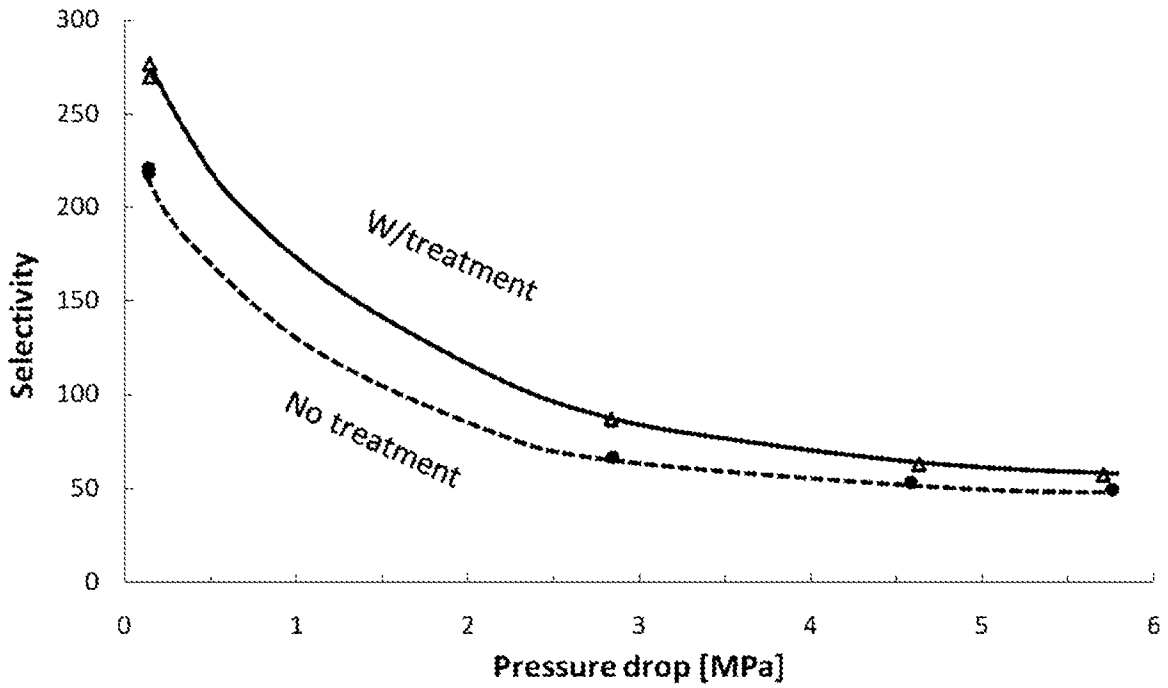


Figure 4a

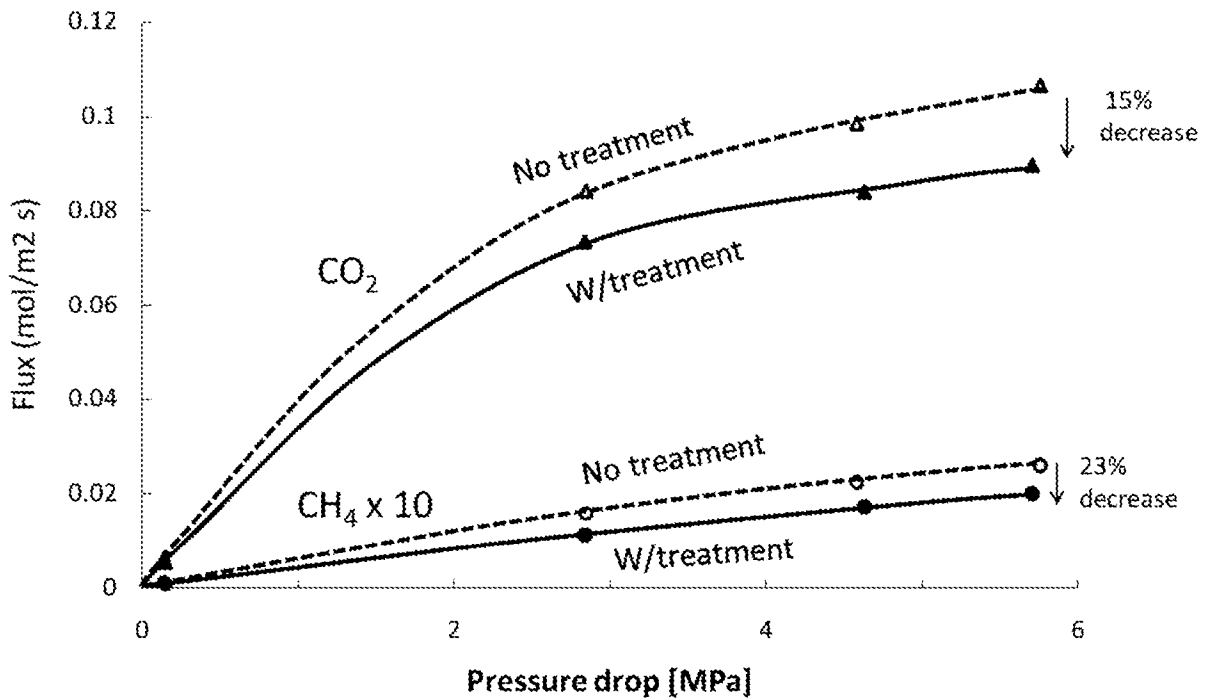


Figure 4b

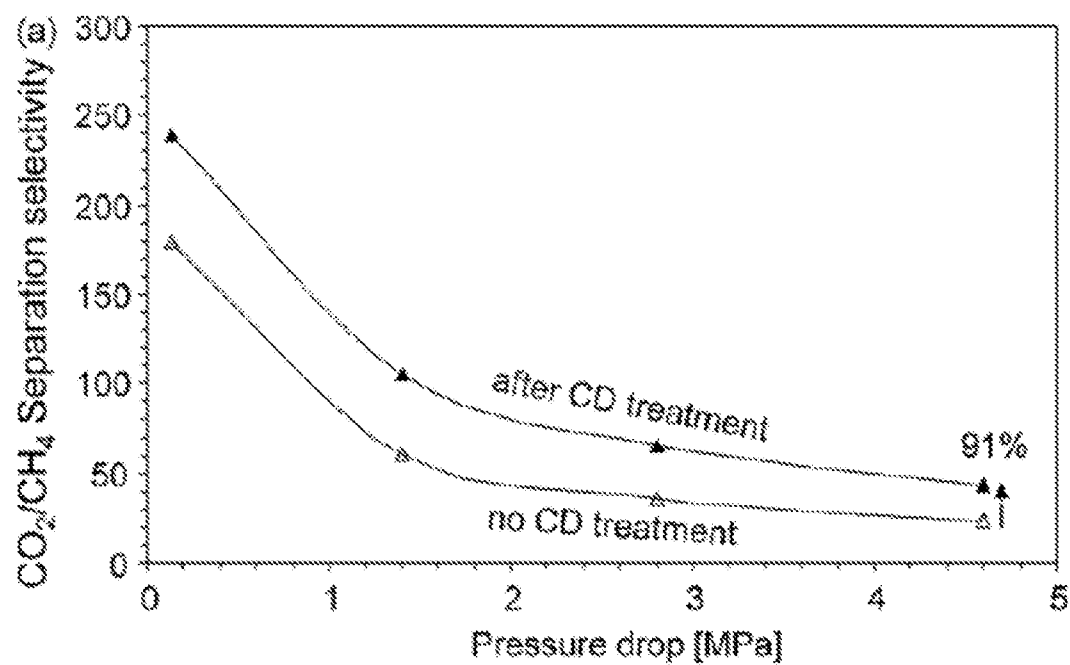


Fig. 5a

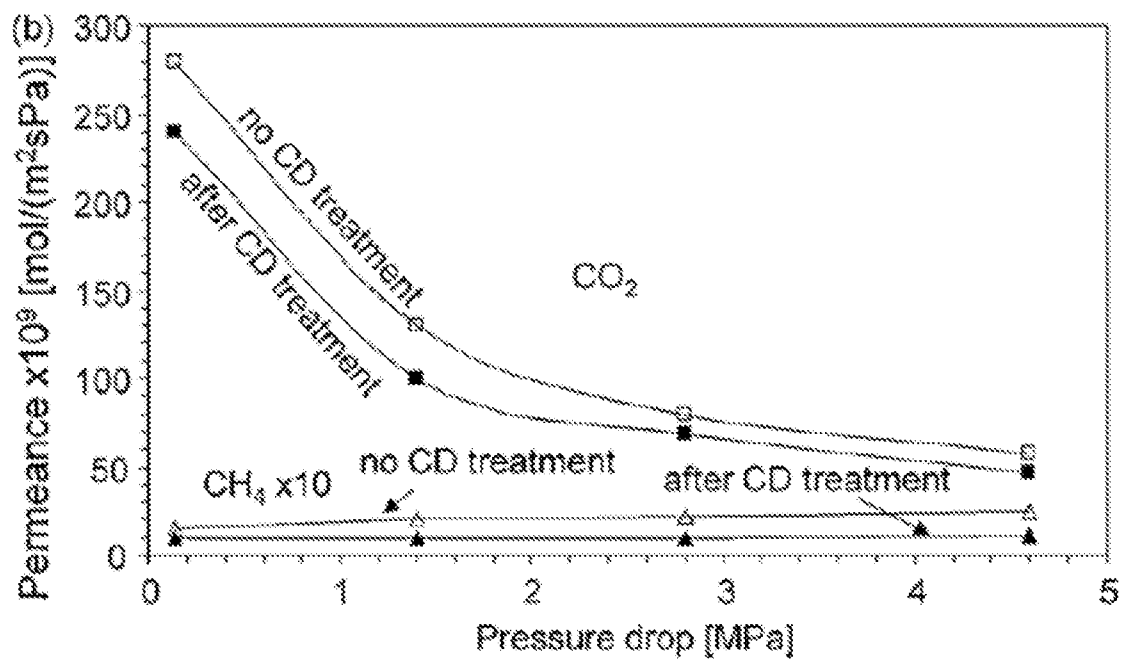


Fig. 5b

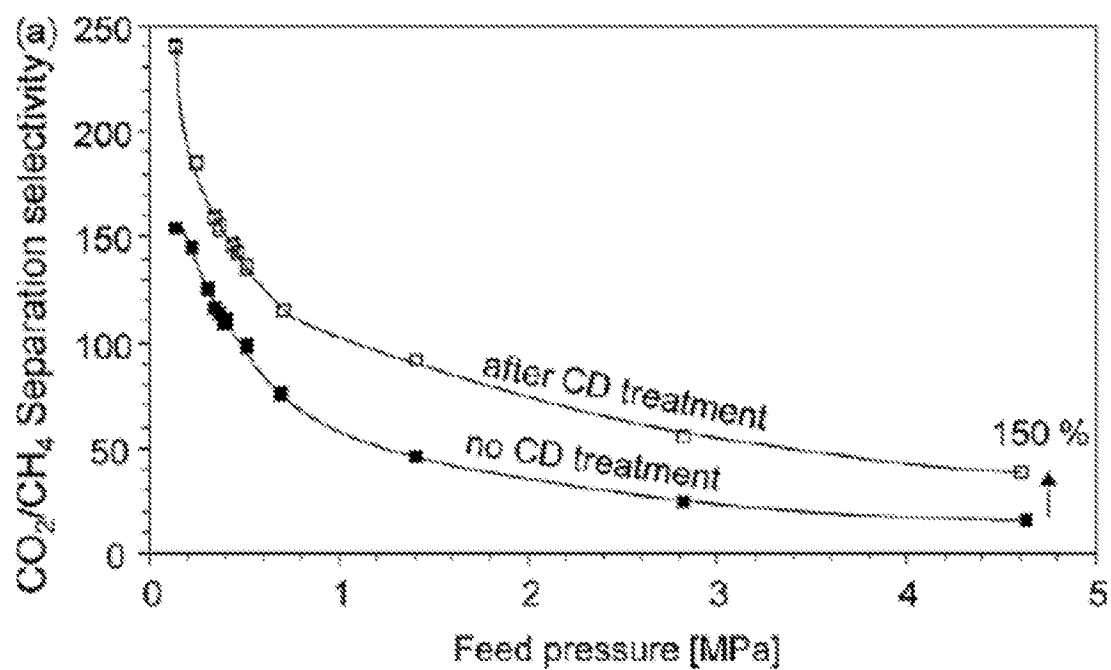


Fig. 6a

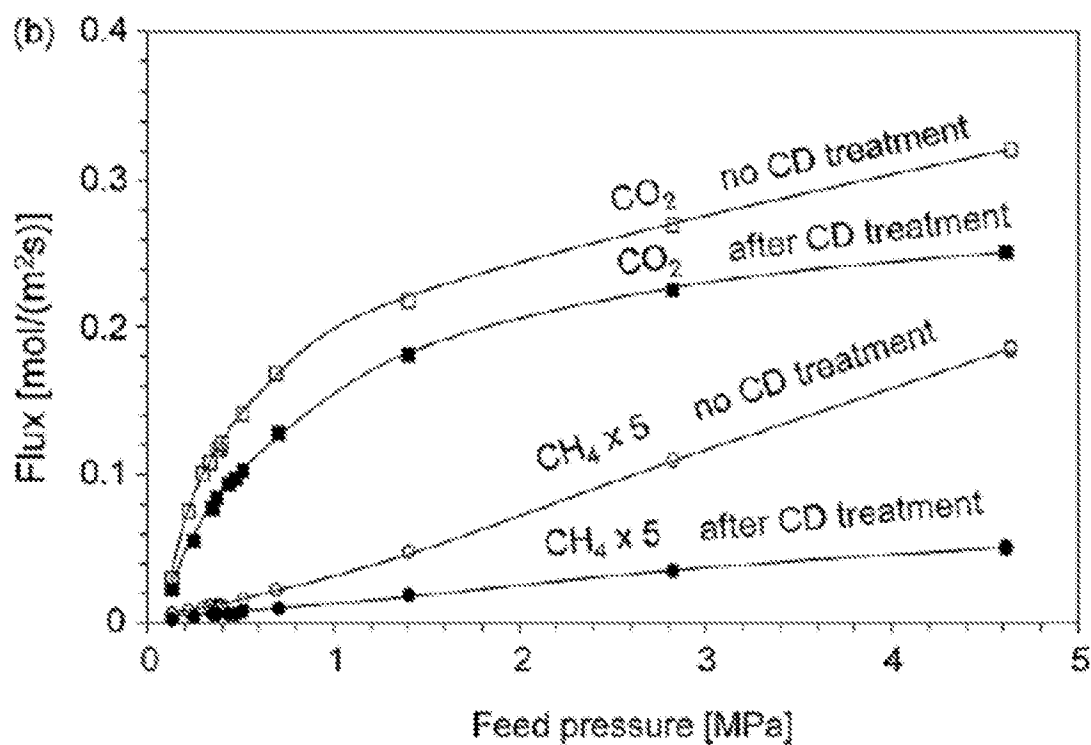


Fig. 6b

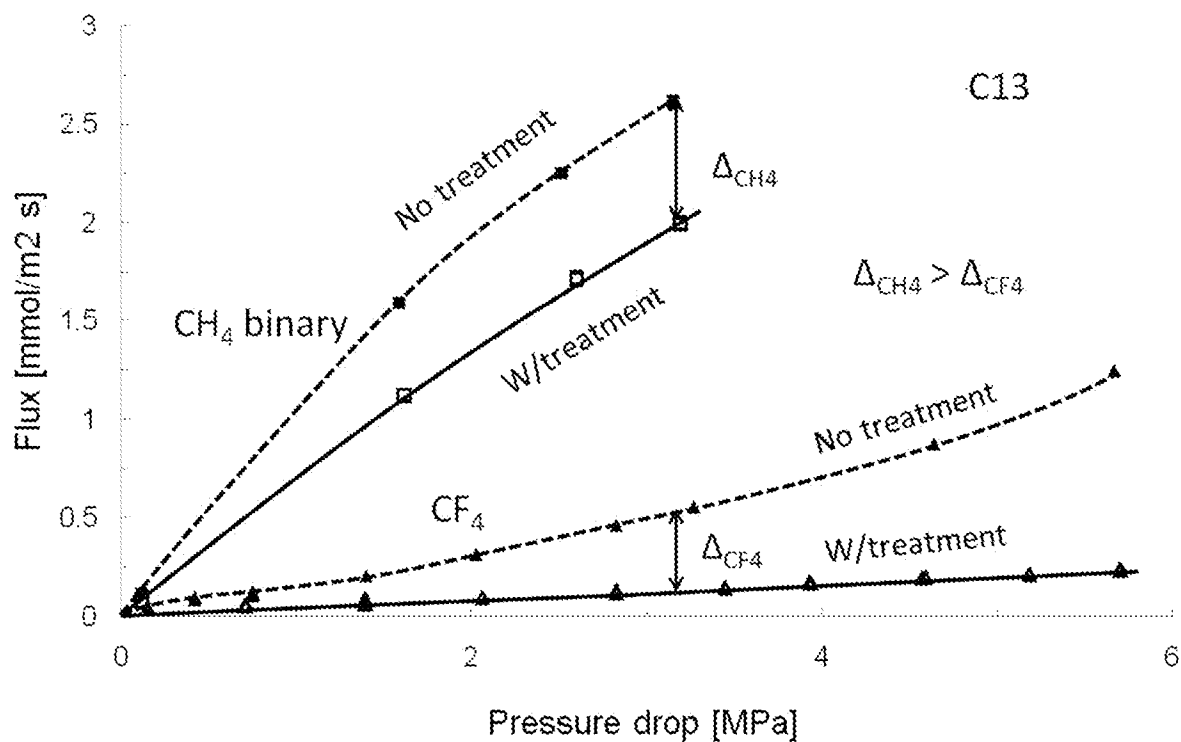


Fig. 7a

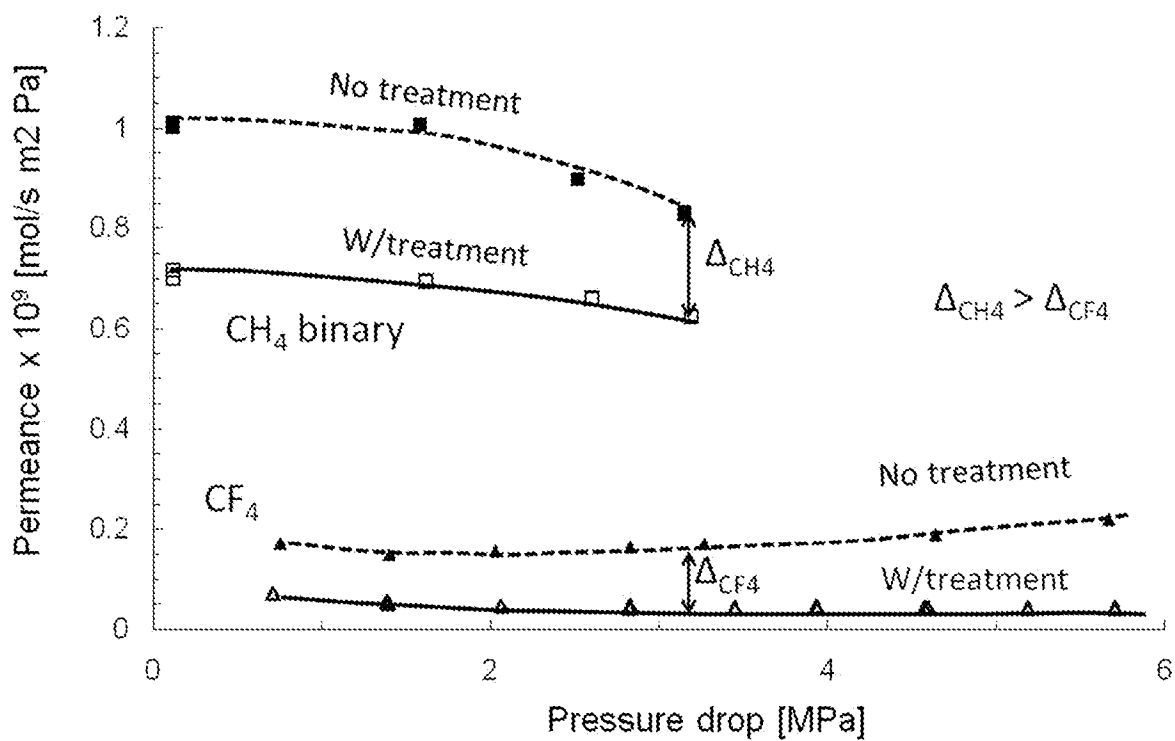


Fig. 7b

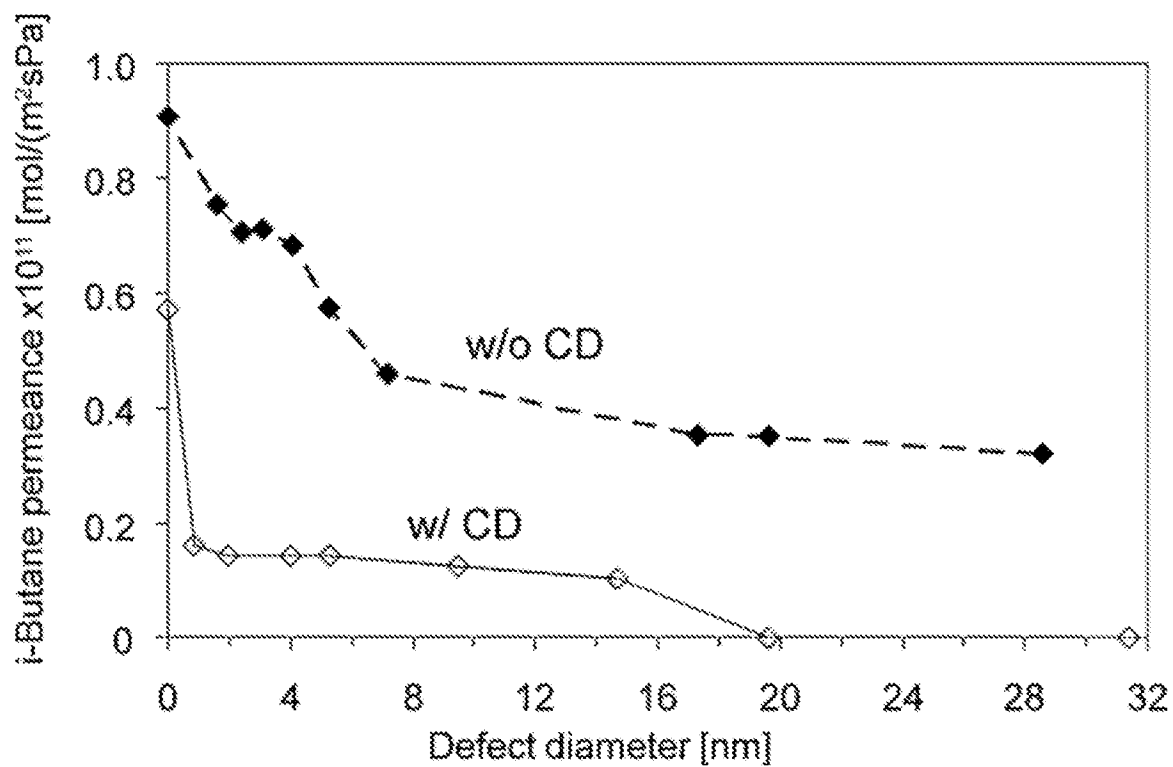


Fig. 8

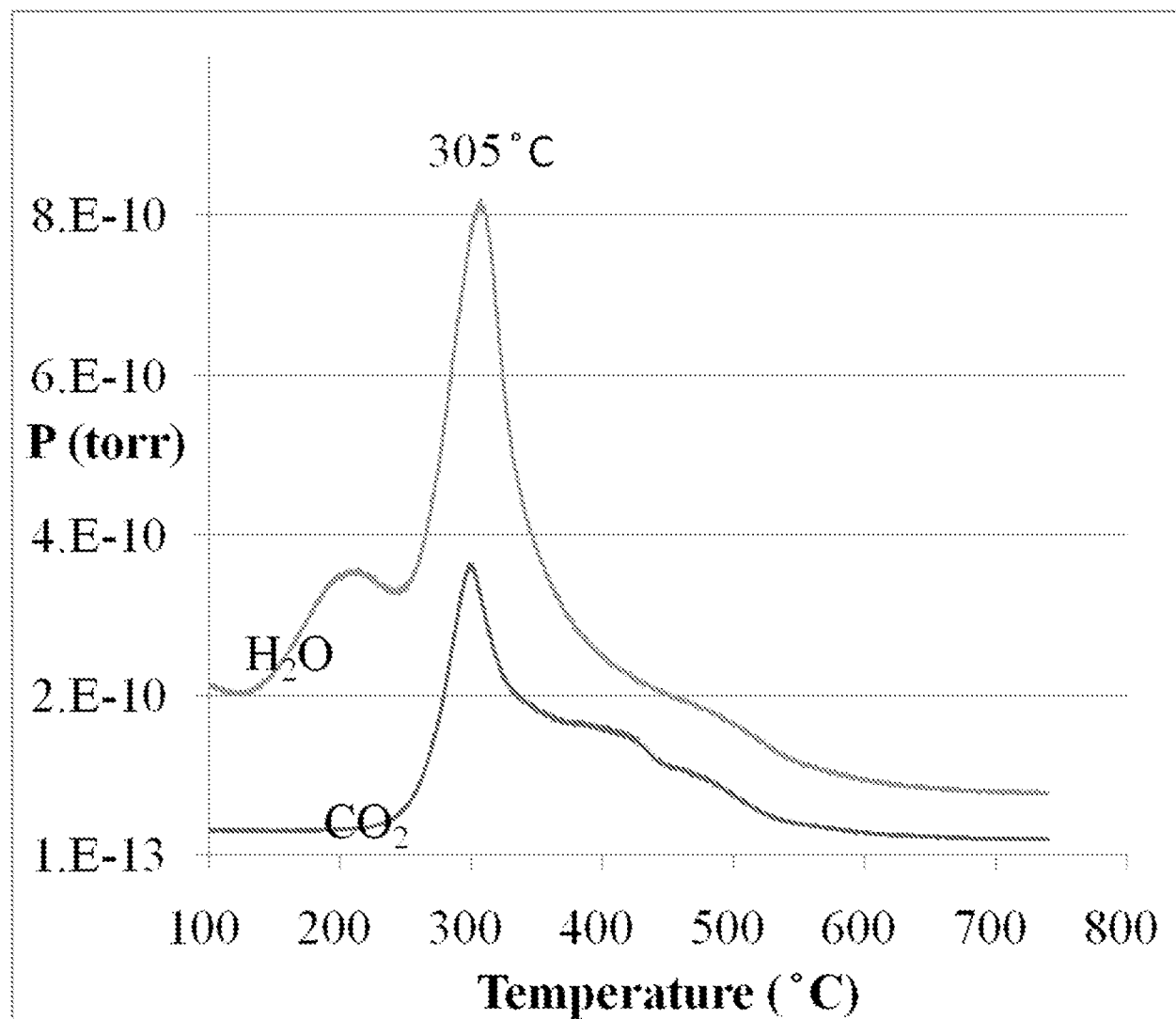


Fig. 9

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A01N 43/04; A61K 31/715 (2010.01)

USPC - 514/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC -- 514/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC -- 424/67, 424/400, 424/401, 424/442, 424/684, 424/724, 514/63, 602/41, 602/45 (see search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST -- PGPB,USPT,USOC,EPAB,JPAB; Dialog Classic Files -- 654, 652, 349, 6, 35, 65, 155; USPTO Web Page, Google Scholar;
Search terms -- calcined, cyclodextrin, molecular sieve, crystalline, zeolite, pores, adsorption, permeation, gas separation, methane, carbon dioxide, pore size, particle size, SAPO-34

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2004/0197278 A1 (GONZALES et al.) 07 October 2004 (07.10.2004) para [0030], [0032], [0042], [0047]-[0050], [0054]-[0055], 0064, [0082]-[0083], [0089], [0134]	1-20
Y	US 2006/0079725 A1 (LI et al.) 13 April 2006 (13.04.2006) para [0013], [0015]-[0016], [0021], [0043], [0044], [0057], [0061]	1-20
Y	US 2005/0204915 A1 (SAMMONS et al.) 22 September 2005 (22.09.2005) para [0018]-[0019], [0112], [0148]	11-16
Y	US 5,714,445 A (TRINH et al.) 03 February 1998 (03.02.1998) col 2, ln 30-43; col 24, ln 31-58	8

☐ Further documents are listed in the continuation of Box C.

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

29 November 2010 (29.11.2010)

Date of mailing of the international search report

08 DEC 2010

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