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(54) **NANO-MOLECULAR SIEVE-POLYMER MIXED MATRIX MEMBRANES WITH SIGNIFICANTLY IMPROVED GAS SEPARATION PERFORMANCE**

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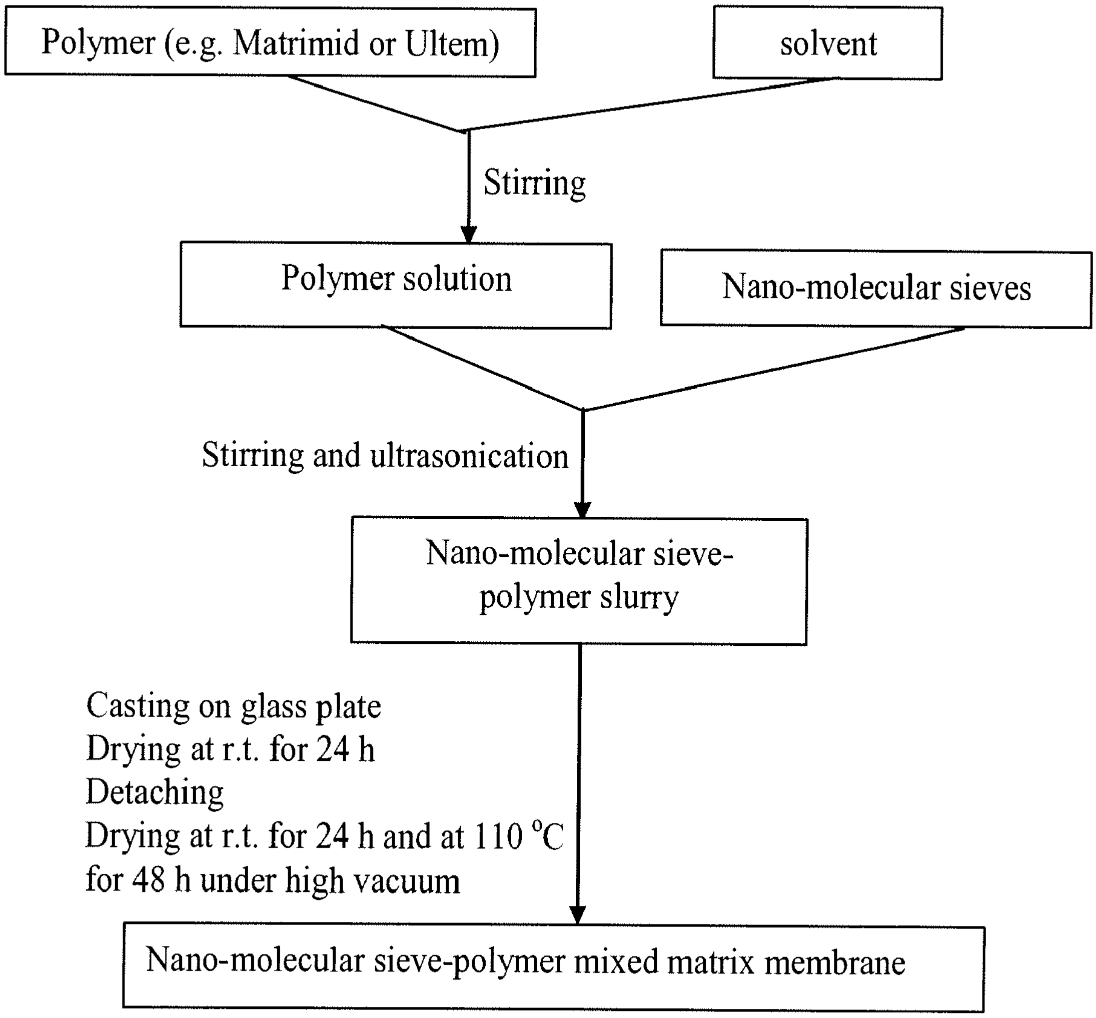
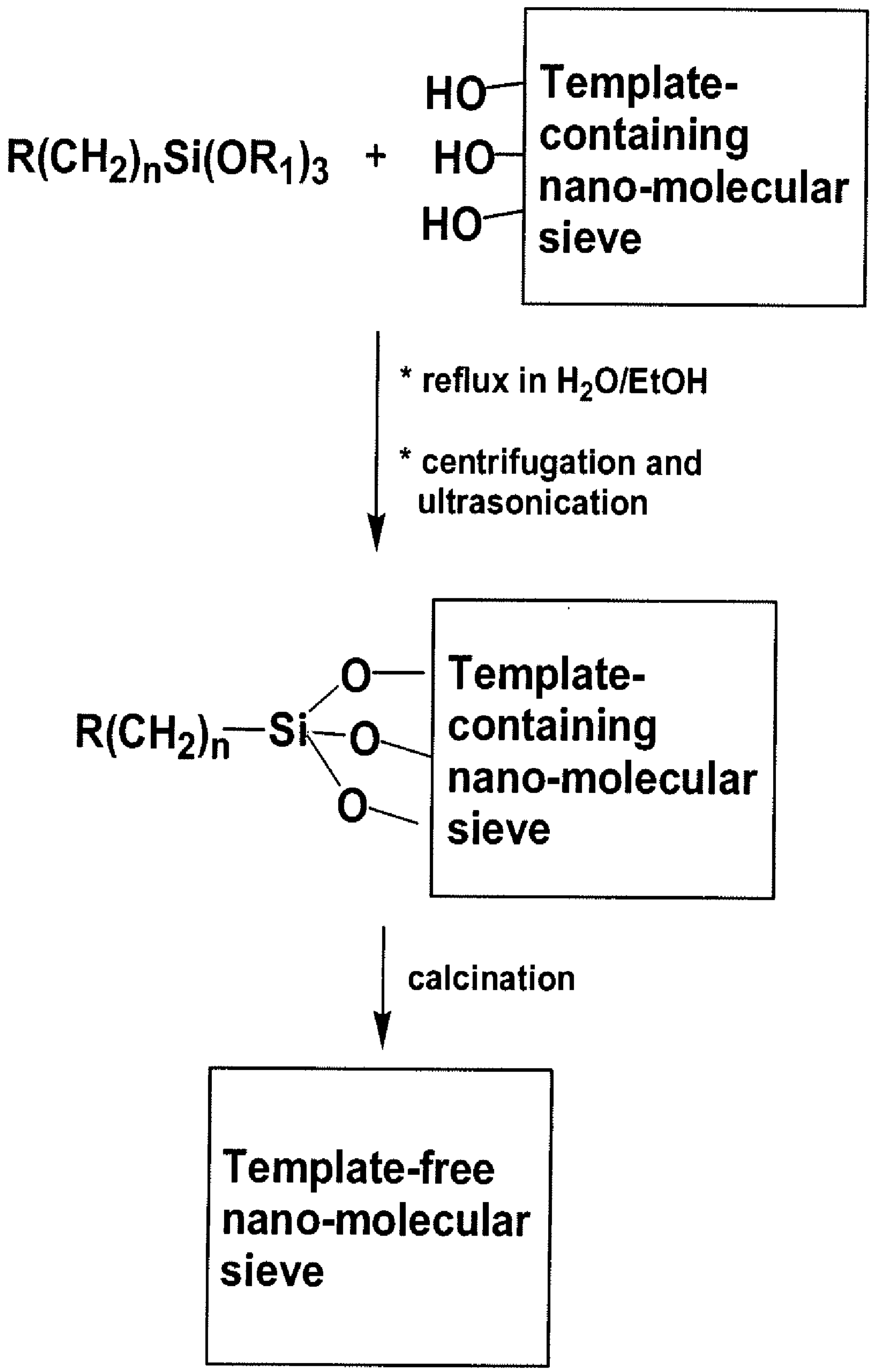
(57) **ABSTRACT**

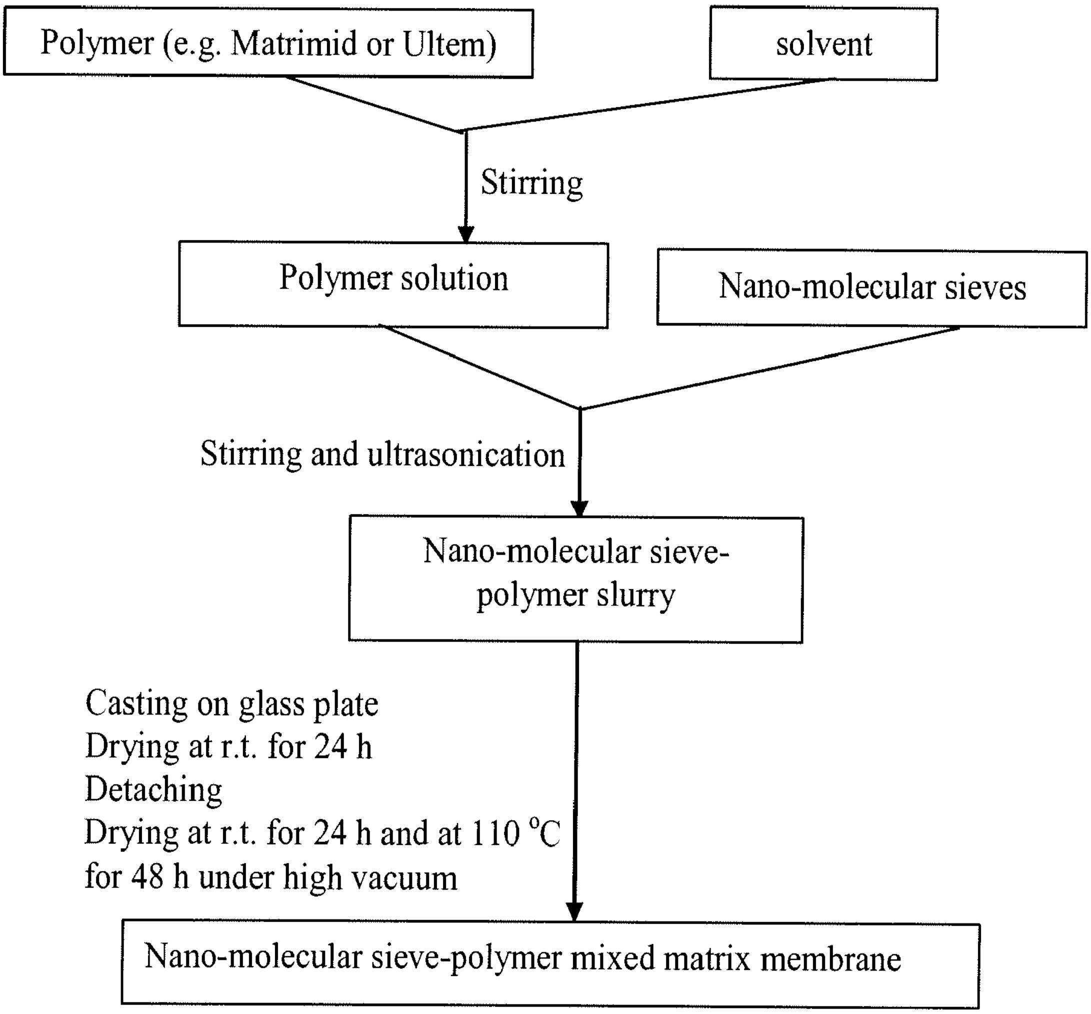
Nano-molecular sieve-polymer mixed matrix membranes (MMMS) for CO_2 removal from natural gas have been prepared by incorporating dispersible template-free nano-molecular sieves into polymer matrices such as Matrimid 5218 polyimide matrix or Ultem 1000 polyetherimide matrix. The nano-molecular sieves used in this invention include template-free nano-AlPO-18, nano-AlPO-5, nano-Silicalite, nano-SAPO-34, and PEG-functionalized nano-Silicalite. These template-free nano-molecular sieves were synthesized by an organic ligand grafting method.





R(CH2)nSi(OR1)3 + HO HO HO
Template-containing nano-molecular sieve
* reflux in H2O/EtOH
* centrifugation and ultrasonication
R(CH2)n—Si O O O
Template-containing nano-molecular sieve
calcination
Template-free nano-molecular sieve

FIG. 1



Polymer (e.g. Matrimid or Ultem)
solvent
Stirring
Polymer solution
Nano-molecular sieves
Stirring and ultrasonication
Nano-molecular sieve-polymer slurry
Casting on glass plate
Drying at r.t. for 24 h
Detaching
Drying at r.t. for 24 h and at 110 °C
for 48 h under high vacuum
Nano-molecular sieve-polymer mixed matrix membrane

FIG. 2

NANO-MOLECULAR SIEVE-POLYMER MIXED MATRIX MEMBRANES WITH SIGNIFICANTLY IMPROVED GAS SEPARATION PERFORMANCE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from Provisional Application Ser. No. 60/781,297 filed Mar. 10, 2006, the contents of which are hereby incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] Gas separation processes with membranes have undergone a major evolution since the introduction of the first membrane-based industrial hydrogen separation process about two decades ago. The design of new materials and efficient methods will further advance the membrane gas separation processes within the next decade.

[0003] The gas transport properties of many glassy and rubbery polymers have been measured, driven by the search for materials with high permeability and high selectivity for potential use as gas separation membranes. Unfortunately, an important limitation in the development of new membranes for gas separation applications is the well-known trade-off between permeability and selectivity, as first shown by Robeson. See Robeson, J. Membr. Sci., 62: 165 (1991); Robeson, Curr. Opin. Solid State Mater. Sci., 4: 549 (1999). By comparing the data of hundreds of different polymers, he demonstrated that selectivity and permeability seem to be inseparably linked to one another, in a relation where selectivity increases as permeability decreases and vice versa.

[0004] Despite concentrated efforts to tailor polymer structure to affect separation properties, current polymeric membrane materials have seemingly reached a limit in the tradeoff between productivity and selectivity. See Zimmerman, et al., J. Membr. Sci., 137: 145 (1997). For example, many polyimide and polyetherimide glassy polymers such as Ultem 1000 have much higher intrinsic CO_2/CH_4 selectivities (~30 at 50° C. and 100 psig) than that of cellulose acetate (CA, ~22), which are more attractive for practical gas separation applications. These polymers, however, do not have outstanding permeabilities attractive for commercialization compared to current UOP Separex CA membrane product, completely in agreement with the Robeson trade-off relation.

[0005] Our previous study has shown that nano-molecular sieves such as poly(ethylene glycol) (PEG)-functionalized nano-Silicalite or nano-SAPO-34 dispersed in CA-based mixed matrix membranes (MMM) can enhance the CO_2 permeability over the intrinsic CO_2 permeability of the pure CA polymer matrix, and in the meantime the CO_2/CH_4 selectivity (**60** $_{CO2/CH4}$) remained almost the same as that of CA polymer matrix. The $\alpha_{CO2/CH4}$ of nano-molecular sieve-CA MMM films (<22), however, is still not high enough for the next generation of UOP Separex membrane product for CO_2 removal from natural gas.

[0006] Therefore, the aim of the present invention is to prepare nano-molecular sieve-polymer MMM membranes to achieve higher $\alpha_{CO2/CH4}$ than that of CA membrane with at least higher than 5 barrer CO_2 permeability, which is promising for practical application. We studied the use of template-free nano-molecular sieves, such as template-free nano-Silicalite, nano-AlPO-18, nano-SAPO-34, and PEG-functionalized nano-Silicalite, as the dispersed phase in MMM films using Matrimid 5218 and Ultem 1000 continuous polymer matrices. Experimental pure gas permeation results demonstrated significantly improved CO_2/CH_4 separation properties.

SUMMARY OF THE INVENTION

[0007] In this invention, new nano-molecular sieve-polymer MMMs for CO_2 removal from natural gas have been prepared by incorporating dispersible template-free nano-molecular sieves into polymer matrices such as Matrimid 5218 polyimide matrix or Ultem 1000 polyetherimide matrix. The nano-molecular sieves used in this invention include template-free nano-AlPO-18, nano-AlPO-14, nano-AlPO-34, nano-UZM-25, nano-CDS-1, nano-Nu-6(2), nano-AlPO-25, nano-AlPO-5, nano-Silicalite, and nano-SAPO-34. These dispersible template-free nano-molecular sieves were synthesized by an organic ligand-grafting-calcination method.

[0008] For nano-AlPO-18-Ultem mixed matrix membrane (MMM) containing 40 wt-% of template-free nano-AlPO-18 molecular sieve particles, pure gas permeation test results show simultaneously improved CO_2/CH_4 selectivity by 19% and CO_2 permeability by about 250% over the pure Ultem polymer membrane.

[0009] For nano-SAPO-34-Ultem MMM with 30 wt-% of template-free nano-SAPO-34 loading, pure gas permeation tests show both improved CO_2 permeability (2.58 barrer) and CO_2/CH_4 selectivity (34.9) compared to the intrinsic CO_2 permeability (1.95 barrer) and CO_2/CH_4 selectivity (30.3) of the pure Ultem polymer matrix. For nano-Silicalite-Ultem MMM film with 30 wt-% of template-free nano-Silicalite loading, pure gas permeation tests show significant enhancement by as much as 260% in CO_2 permeability over the intrinsic CO_2 permeability of the pure Ultem polymer matrix with equal CO_2/CH_4 selectivity. Likewise, for nano-Silicalite-Matrimid MMM with 30 wt-% of template-free nano-Silicalite loading, enhancement by as much as 93% in CO_2 permeability and slightly increased CO_2/CH_4 selectivity were observed.

[0010] These nano-AlPO-18-Ultem, nano-SAPO-34-Ultem, nano-Silicalite-Ultem and nano-Silicalite-Matrimid MMMs have significantly improved performance with outstanding permeabilities and high CO_2/CH_4 selectivities (>29) compared to current Separex CA membrane (~22 $CO2/CH_4$ selectivity) for CO_2 removal from natural gas, which makes them very promising membrane candidates for CO_2 removal from natural gas.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. **1** shows the synthesis of template-free nano-molecular sieves using an organic ligand grafting-calcination method.

[0012] FIG. **2** shows a preparation flowchart of a nano-molecular sieve-polymer mixed matrix membrane.

DETAILED DESCRIPTION OF THE INVENTION

[0013] In our previous work, dispersible template-free nano-molecular sieves such as nano-Silicalite and nano-SAPO-34 were synthesized by an organic ligand-grafting-calcination method. The incorporation of the template-free nano-molecular sieves into a 1:1 weight ratio CA/CTA blend polymer matrix (cellulose acetate/cellulose triacetate) was investigated as a way to improve the gas separation properties (permeability of CO_2 and selectivity of CO_2/CH_4) of the CA/CTA polymer materials. The loading of the nano-molecular sieves in the nano-molecular sieve-polymer mixed matrix membranes (MMMs) was varied from 0 to 40 wt-%.

[0014] The permeability (P_{CO2}) and selectivity ($\alpha_{CO2/CH4}$) of some of the nano-molecular sieve-CA MMMs have been tested by pure gas measurements at 50° C. under 690 kPa (100 psig) single gas pressure. For all the gases tested (N_2, H_2, He, CO_2 and CH_4), MMMs containing PEG-nano-Silicalite, PEG-nano-SAPO-34, and nano-SAPO-34 show dramatically increased permeability (e.g., P_{CO2} increase of 15 to 79%) over that of pure CA membrane. At the same time, the calculated ideal selectivity ($\alpha_{CO2/CH4}$) remained almost the same or only slight decreased. It has been confirmed that the significant increase in permeability is attributed to intrinsic gas transport properties and not to the defects in the films. In addition, the mechanical strength of the MMMs with up to 30 wt-% nano-molecular sieve loading is still strong enough to hold 690 kPa (100 psig) testing pressure.

[0015] These encouraging results suggest that PEG-nano-Silicalite, PEG-nano-SAPO-34, and nano-SAPO-34 are attractive additives for universally enhancing the gas permeability of CA without sacrificing $\alpha_{CO2/CH4}$. These results also indicate that the relative hydrophilicity of the nano-molecular sieves (such as the existence of PEG groups, Al, and P) plays a key role for enhancing the dispersity of the nano-molecular sieves in the CA polymer matrix and improving the adhesion between the nano-molecular sieves and the polymer. The $\alpha_{CO2/CH4}$ of nano-molecular sieve-CA MMMs (<22), however, is still not high enough for the next generation of membrane product for CO_2 removal from natural gas.

[0016] Therefore, the aim of the present invention is to prepare nano-molecular sieve-polymer MMMs to achieve higher $\alpha_{CO2/CH4}$ than that of CA membrane with equal or slightly lower CO_2 permeability, which is promising for practical application.

[0017] In this invention, we achieve higher $\alpha_{CO2/CH4}$ with equal or slightly lower P_{CO2} compared to those of CA membrane (P_{CO2}=~8 barrers and $\alpha_{CO2/CH4}$=~22 at 50° C. and 690 kPa (100 psig)) taking advantage of the intrinsic gas transport properties of both appropriate nano-molecular sieves (or modified nano-molecular sieves) and polymer material (for example, some glassy polymers such as polyimides (PIs) and polyetherimides (PEIs) have much higher $\alpha_{CO2/CH4}$ than CA polymer, but their permeabilities are too low to be of commercial interest). PIs and PEIs are relatively hydrophobic glassy polymers. With the incorporation of nano-molecular sieves with suitable hydrophobicity, it is possible to increase the P_{CO2} and maintain the high $\alpha_{CO2/CH4}$ of PI or PEI polymers, so that both the $\alpha_{CO2/CH4}$ and P_{CO2} could be much higher than those of CA polymer material.

1) Preparation of MMMs

[0018] In this work, new nano-molecular sieve-polymer MMMs for CO_2 removal from natural gas have been prepared by incorporating dispersible template-free nano-molecular sieves into polymer matrices such as Matrimid 5218 polyimide matrix or Ultem 1000 polyetherimide matrix (Table 1). The nano-molecular sieves used in this invention include template-free nano-AlPO-18, nano-AlPO-14, nano-AlPO-34, nano-UZM-25, nano-CDS-1, nano-Nu-6(2), nano-AlPO-25, nano-AlPO-5, nano-Silicalite, and nano-SAPO-34. These dispersible template-free nano-molecular sieves were synthesized by an organic ligand-grafting-calcination method as shown in FIG. **1**.

[0019] MMMs were prepared from solution casting of template-free nano-molecular sieve particles dispersed in a solution of Matrimid 5218 or Ultem 1000 polymer (FIG. **2**). The loading of the nano-molecular sieves in the MMMs is in a range of 5 wt-% to 70 wt-% (i.e., nano-molecular sieve/polymer=5 wt-%–70 wt-%). Matrimid 5218 or Ultem 1000 polymer was dissolved in an organic solvent such as methylene chloride or a mixture of several organic solvents at room temperature to form a homogeneous polymer solution. A measured amount of dry template-free nano-molecular sieves was then added, and the resulting slurry was stirred and ultrasonicated for three times to ensure good dispersion of the template-free nano-molecular sieves. The Matrimid 5218 or Ultem 1000 solution containing dispersed template-free nano-molecular sieves was poured into a glass ring on top of a clean glass plate, and dried at room temperature for 24 hours. The resulting dried MMMs were detached from the glass plate and were further dried at room temperature for at least 24 hours and then at 110° C. for at least 48 hours under high vacuum. The MMMs were around 1-3 mils thick, measured with a micrometer. They were cut into small circles for gas separation measurements.

2) MMM Gas Separation Tests

[0020] The permeabilities of CO_2 and CH_4 (P) and selectivity for CO_2/CH_4 ($\alpha_{CO2/CH4}$) of the nano-molecular sieve-polymer MMMs were measured by pure gas measurements at 50° C. under 690 kPa (100 psig) pressure.

[0021] For nano-AlPO-18-Ultem mixed matrix membrane (MMM) containing 40 wt-% of template-free nano-AlPO-18 molecular sieve particles, pure gas permeation test results (Table 2) showed simultaneously improved CO_2/CH_4 selectivity by 19% and CO_2 permeability by about 250% over the pure Ultem polymer membrane, indicating a successful combination of molecular sieving and sorption mechanism of nano-AlPO-18 molecular sieve fillers with solution-diffusion mechanism of Ultem polymer matrix in this nano-AlPO-18-Ultem MMM for CO_2/CH_4 separation.

[0022] For nano-SAPO-34-Ultem MMM film with 30 wt-% of nano-SAPO-34 loading, pure gas permeation tests (Table 2) show both improved CO_2 permeability (2.58 barrer) and CO_2/CH_4 selectivity (34.9) compared to the intrinsic CO_2 permeability (1.95 barrer) and CO_2/CH_4 selectivity (30.3) of the pure Ultem polymer matrix. For nano-Silicalite-Ultem MMM film with 30 wt-% of nano-Silicalite loading, pure gas permeation tests (Table 2) show significant enhancement by as much as 260% in CO_2 permeability over the intrinsic CO_2 permeability of the pure Ultem polymer matrix with equal CO_2/CH_4 selectivity. Both nano-Silicalite and nano-SAPO-34 can be uniformly dispersed in Matrimid and Ultem polymer matrices. However, nano-zeolite PEG-nano-Silicalite with hydrophilic PEG groups on their surfaces cannot disperse very well in either Matrimid or Ultem matrix. Pure gas permeation tests (Table 2) show increased CO_2 permeability (4.87 barrer), but the CO_2/CH_4 selectivity slightly decreased as compared to that of the pure Ultem polymer matrix. These results indicate that the compactibility and dispersity of the nano-molecular sieves with the polymer matrices plays a key role for the enhancement of gas separation properties of the MMMs. These encouraging selectivity and permeability enhancements prove the concept of MMM and confirm that MMM behavior is achievable with appropriate nano-molecular sieves.

[0023] Likewise, for nano-Silicalite-Matrimid and nano-SAPO-34-Matrimid MMMs with 30 wt-% of nano-Silicalite and nano-SAPO-34 loading, respectively, enhancements by as much as 93% in CO_2 permeability for nano-Silicalite-Matrimid and by as much as 69% in CO_2 permeability for nano-SAPO-34-Matrimid were observed with slightly increased CO_2/CH_4 selectivity compared to those of the pure Matrimid matrix (Table 3).

[0024] These nano-AlPO-18-Ultem, nano-SAPO-34-Ultem, nano-Silicalite-Ultem, nano-SAPO-34-Matrimid and nano-Silicalite-Matrimid MMMs have significantly improved performance with outstanding permeabilities and high CO_2/CH_4 selectivities compared to current Separex CA and CAP membranes (~22 CO_2/CH_4 selectivity) for CO_2 removal from natural gas, which makes them very promising membrane candidates for CO_2 removal from natural gas.

TABLE 3

Pure gas permeation properties of nano-molecular sieve-Matrimid mixed matrix membranes using Matrimid 5218 as polymer matrix*

	Permeability (P, barrer)			Selectivity	
Membrane	P_{CO2}	P_{CO2} increased	P_{CH4}	$\alpha_{CO2/CH4}$	$\alpha_{CO2/CH4}$ increased
Pure Matrimid 5218	10.0	0	0.355	28.2	0
30%-nano-Silicalite-Matrimid	19.3	93%	0.663	29.1	3.2%
30%-PEG-nano-Silicalite-Matrimid	18.8	88%	0.723	26.0	−7.8%

TABLE 1

Chemical structures and physical properties of Matrimid 5218 and Ultem 1000 polymers

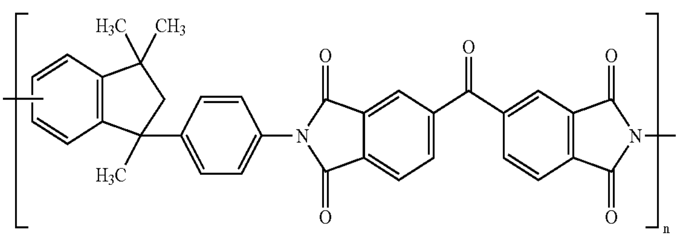
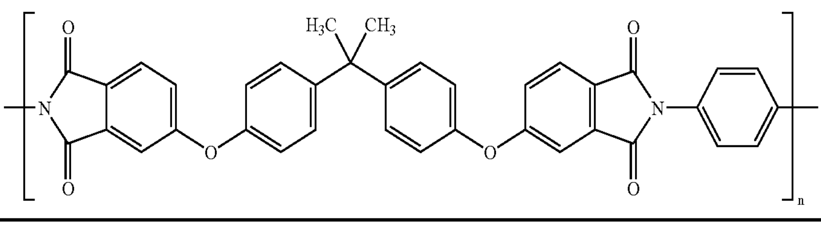
Polymer	Chemical structure	Density (g/cm³)	T_g (° C.)
Matrimid 5218		1.24	302
Ultem 1000		1.27	209

TABLE 2

Pure gas permeation properties of nano-molecular sieve-Ultem mixed matrix membranes using Ultem 1000 as polymer matrix*

	Permeability (P, barrer)			Selectivity	
Membrane	P_{CO2}	P_{CO2} increased	P_{CH4}	$\alpha_{CO2/CH4}$	$\alpha_{CO2/CH4}$ increased
Pure Ultem 1000	1.95	0	0.0644	30.3	0
40%-nano-AlPO-18-Ultem	6.74	246%	0.187	36.0	18.8%
30%-nano-Silicalite-Ultem	7.05	261%	0.232	30.4	0.3%
30%-PEG-nano-Silicalite-Ultem	4.87	151%	0.170	28.6	−5.6%
30%-nano-SAPO-34-Ultem	2.58	32%	0.0739	34.9	15.2%

*Testing conditions: Pure gas permeation, 50° C., 690 kPa (100 psig); 1 barrer = 10^{-10} cm^3(STP) · cm/cm^2 · sec · cmHg

TABLE 3-continued

Pure gas permeation properties of nano-molecular sieve-Matrimid mixed matrix membranes using Matrimid 5218 as polymer matrix*

	Permeability (P, barrer)			Selectivity	
Membrane	P_{CO2}	P_{CO2} increased	P_{CH4}	$\alpha_{CO2/CH4}$	$\alpha_{CO2/CH4}$ increased
30%-nano-SAPO-34-Matrimid	16.9	69%	0.592	28.6	1.4%

*Testing conditions: Pure gas permeation, 50° C., 690 kPa (100 psig); 1 barrer = 10^{-10} cm^3(STP) · cm/cm^2 · sec · cmHg

1. A method of manufacturing a membrane comprising:

(a) selecting a quantity of one or more types of template-containing nano-molecular sieve particles;

(b) functionalizing said template-containing nano-molecular sieve particles by grafting an organic functional group on an outer surface of said template-containing nano-molecular sieve particles using a functional organic linkage;

(c) making template-free nano-molecular sieve particles by high temperature calcination of the said functionalized template-containing nano-molecular sieve particles;

(d) forming a mixture by mixing 5 to 70 wt-% of said template-free nano-molecular sieve particles with a polyimide or polyetherimide polymer; and

(e) making a membrane from said mixture.

2. The method of claim **1** wherein said nano-molecular sieve particles have a particle size from 5 to 1000 nm.

3. The method of claim **1** wherein said nano-molecular sieve particles are selected from the group consisting of nano-AlPO-18, nano-AlPO-14, nano-AlPO-34, nano-UZM-25, nano-CDS-1, nano-Nu-6(2), nano-AlPO-25, nano-AlPO-5, nano-Silicalite, and nano-SAPO-34.

4. The method of claim **1** wherein said functional organic linkage is an organosilane.

5. The method of claim **1** wherein said functional organic linkage is a compound having the formula $R(CH_2)_nSi(OR_1)_3$ in which R is an organic functional group, n is an integer from 1 to 20, and R_1 is a C_1-C_8 hydrocarbon group.

6. The method of claim **1** wherein said functional organic linkage is a compound having the formula $R(CH_2)_nSiR'(OR_1)_2$ in which R is an organic functional group, n is an integer from 1 to 20, R_1 is a C_1-C_8 hydrocarbon group, and R' is a C_1-C_8 hydrocarbon group.

7. The method of claim **1** wherein said functional organic linkage is a compound having the formula $R(CH_2)_nSiR'(R'')(OR_1)$ in which R is an organic functional group, n is an integer from 1 to 20, R_1 is a C_1-C_8 hydrocarbon group, R' is a C_1-C_8 hydrocarbon group, and R'' is a C_1-C_8 hydrocarbon group.

8. The method of claim **1** wherein said surface-functionalized molecular sieve nanoparticles are dispersible in organic solvents.

9. A mixed matrix membrane made by the method of claim **1**.

10. A mixed matrix membrane comprising a mixture of:

(a) one or more continuous phase polyetherimide or polyimide polymers; and

(b) dispersed therein template-free nano-molecular sieve particles.

11. The mixed matrix membrane of claim **10** wherein said nano-molecular sieve particles are selected from the group consisting of nano-AlPO-18, nano-AlPO-14, nano-AlPO-34, nano-UZM-25, nano-CDS-1, nano-Nu-6(2), nano-AlPO-25, nano-AlPO-5, nano-Silicalite, and nano-SAPO-34.

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