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Hans汉斯

乙酸渗透汽化脱水膜的研究进展

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摘　要

乙酸是一种重要的化工原料，可以广泛地应用在医药、染料、农药、合成纤维等各个行业。我国是目前世界上最大的乙酸生产国，但在乙酸生产的过程中有副产物水生成，因此乙酸脱水是其生产过程中不可缺少的环节。相对于传统的精馏技术，膜渗透汽化脱水具有效率高、操作简单、能耗低等优势，在乙酸脱水中具有广阔的应用前景。本文总结了近年来用于乙酸脱水渗透汽化膜的研究进展，主要从膜材料及其分离性能方面对现有乙酸渗透汽化脱水膜进行了分析。最后，对乙酸脱水膜的发展前景做出了展望。

关键词

乙酸脱水，渗透汽化，膜分离

Research Progress of Acetic Acid Pervaporation Dehydration Membrane

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Abstract

Acetic acid is an important chemical raw material, which can be widely used in medicine, dyes, pesticides, synthetic fiber and other industries. At present, China is the largest producer of acetic acid in the world, but there is by-product water formation in the process of acetic acid production, so acetic acid dehydration is an indispensable link in its production process. Compared with the traditional distillation technology, membrane pervaporation dehydration has the advantages of high efficiency, simple operation and low energy consumption, so it has a broad application prospect in acetic acid dehydration. This paper summarizes the research progress of acetic acid dehydration pervaporation membranes in recent years, and mainly analyzes the existing acetic acid pervaporation membranes from the aspects of membrane materials and separation performance. Finally, the development prospect of acetic acid dehydration membrane is prospected.

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Keywords

Water Removal from Acetic Acid, Pervaporation, Membrane Separation

1. 引言

乙酸是目前世界上需求量最大的化工产品之一，主要用于生产醋酸乙烯酯单体、对苯二甲酸、热熔胶等产品，已广泛应用于医药、染料、农药、合成纤维等行业[1]。但是乙酸在生产过程中常常伴随着水的产生。因此，乙酸脱水是生产高附加值化学品的必要工艺。目前，工业上主要采用精馏法、吸附法、萃取法等方式实现乙酸和水的分离[2] [3]。但由于乙酸和水的缔合作用强，采用精馏等工艺存在着成本高、能耗高、后期处理困难且污染环境等问题。因此，开发新型、环保、节能的乙酸脱水技术势在必行。

渗透汽化(PV)膜分离被认为是一种潜在的节能技术，具有操作简单、分离效率高、能源消耗低和环保等优点，可广泛应用于溶剂回收、有机物分离、海水淡化、制药和食品工业等领域[4]。一般来说，渗透汽化可以分离一些近沸点混合物和低浓度的热敏物质，如乙醇－水、异丙醇－水以及乙酸－水。其传质过程有多种模型，对于有机物膜，溶解－扩散模型是最为广泛接受的。各组分在膜中的传质可以分为三个阶段：1) 溶解，料液中的各个组分在膜表面发生选择性的吸附溶解；2) 扩散，吸附在膜表面的组分通过分子的形式透过膜层，向膜的下游侧扩散；3) 脱附，靠近膜下表面的组分分子在较低的压力条件下发生相变，汽化脱附。对于沸石分子筛膜来说，被广泛接受的是分子筛分机理。通常用分离因子(α)和渗透通量(J) [5]描述复合膜的渗透汽化性能，计算公式如下：

$$\alpha = \frac{y_i / y_j}{x_i / x_j} \tag{1}$$

$$J = \frac{\Delta M}{A \times \Delta t} \tag{2}$$

其中，x_i 和 x_j、y_i 和 y_j 分别为水和乙酸在进料液和渗透液中的质量分数，ΔM 为渗透液的质量，A 为膜的有效面积，Δt 为运行时间。

渗透汽化技术在分离液体混合物时，可以突破传统分离技术的限制，实现有效分离，具有巨大的优势和发展潜力。因此，高效分离乙酸和水混合物的渗透汽化膜已然成为了膜分离领域的热点和前沿之一。本文从膜材料及其渗透汽化分离性能方面总结近年来乙酸脱水膜的研究进展，并分析了乙酸脱水膜面临的挑战及发展前景。

2. 渗透汽化乙酸脱水膜材料

2.1. 聚合物膜

高分子膜材料从 20 世纪 90 年代开始进入化学工业，在渗透汽化回收有机溶剂方面取得了巨大的进展。近年来，它们作为有机混合物脱水的膜材料被广泛研究。聚合物膜具有热稳定的刚性骨架结构[6]，通过选择性吸附目标组分[7]，从而实现混合物的有效分离。优先透水的亲水性聚合物膜(如 PVA)在渗透

汽化乙酸脱水过程中，稳定性较差，溶胀度高导致膜的自由体积增大，膜的分离性能急剧下降。为了减小聚合物膜在水中的溶胀，往往需要通过化学改性或物理改性的方法制备具有优异稳定性的乙酸脱水膜[8] [9]。此外，聚苯并咪唑(PBI) [10]、聚-4 甲基-1 戊烯(TPX) [11] [12]、聚(2,6-二甲基-1,4-苯基氧化物(PPO) [13] [14]等材料也被用于制备乙酸渗透汽化脱水膜。

磺化聚醚酮(SPEKC)具有优良的耐溶剂性、较高的机械性能及热稳定性，Chen 等人[15]将其与 PVA 混合用于渗透汽化乙酸脱水，发现膜的溶胀度随着 SPEKC 含量的增加而降低，从而使膜的稳定性升高。在 50℃，进料液中乙酸为 90wt%时，膜的通量和分离因子分别为 0.492 $kg·m^{-2}·h^{-1}$ 和 59.8。Lee 等人[16]采用戊二醛交联 PVA 膜，当进料液中乙酸为 90wt%时，膜的渗透通量为 0.029 $kg·m^{-2}·h^{-1}$，分离因子为 420。随后，他们通过将氧化石墨烯(GO)纳米片加入到 PVA 基质中增加膜的渗透通量。实验发现，当 PVA 中掺杂 8 wt%氧化石墨烯纳米片时，该膜在乙酸脱水过程中的渗透通量得到明显的提高[17]。尽管大多数亲水性聚合物膜在乙酸脱水中起着至关重要的作用，但这些膜的耐酸性仍有待提高。近年来，聚苯砜(PPSU)因具有良好的热稳定性和化学稳定性而被广泛关注。2011 年 Jullok 等人将 PPSU 膜应用于乙酸脱水，该膜在较高温度及乙酸浓度下都表现出优异的稳定性。

随着膜技术发展到新的水平，大多数用于乙酸脱水的膜材料都是在中空纤维管式载体上开发的，从而获得更高的渗透通量。Zhou 等人[18]以 Matrimid 中空纤维膜为载体，通过在其管道中制备一层致密的分离层而用于乙酸脱水。实验发现，在 101.5℃，进料液中乙酸含量为 20wt%时，该膜的渗透通量可达 1.9 $kg·m^{-2}·h^{-1}$，分离因子约为 95。近年来，人们通过对高分子材料的不断改性以获得更高的分离性能。表 1 列出了聚合物膜分离乙酸和水的 PV 性能。

Table 1. Comparison of PV performance of polymeric membranes for separation acetic/acid mixtures
表 1. 聚合物膜分离乙酸和水混合物的 PV 性能比较

膜	乙酸/水混合物(wt%)	T(℃)	通量/J ($kg·m^{-2}·h·^{-1}$)	分离因子 α	参考文献
PVA/ SA	90-10	33	0.049	21.5	[19]
PVA/SPECK	90-10	50	0.492	59.3	[15]
SPEK-C	90-10	50	0.248	103	[20]
	90-10	20	0.079	153.13	
PVA/MA	90-10	40	0.048	670	[21]
PVA/AN	90-10	30	0.090	14.60	[22]
PVA/PAA	80-20	40	0.040	75.8	[23]
PVA/PAA/0.75MAg	80-20	40	0.140	27	
PVC	50-50	40	6.000	45	[24]
SPBI	90-10	22	0.098	24,000	[25]
PPSU	90-10	80	0.480	12	[21]
PANMA	99.5-0.5	30	1.709	408.91	[1]
	91.5-8.5	30	4.375	35.98	

2.2. 无机膜

无机膜一般由金属、陶瓷、沸石等材料制成，通常以高机械强度、高热稳定性和高化学稳定性闻名，这使得无机膜在苛刻的应用条件中有别于传统的聚合物膜。考虑到乙酸渗透汽化脱水对膜的亲水性和耐

酸性的要求，沸石膜是满足这一挑战的代表性无机膜。在早期的研究中，ZSM-5 沸石膜[26] [27]、A 型沸石膜[28] [29]、Y 型沸石膜[30]和 MOR 沸石膜[31] [32]等已经被应用于有机溶剂渗透汽化脱水的过程中。

沸石是由[SiO_4]和[AlO_4]四面体相互连接而形成的微孔晶体铝硅酸盐材料，其具有均匀、规则的孔道结构及可调节的分子筛骨架硅铝比(SAR) [33]。通常，沸石膜的分离性能和稳定性很大程度上取决于 SAR。根据沸石分子筛的 SAR 值，沸石分子筛膜可分为三类：1) SAR 值为 1.0~1.5 的低 SAR 膜；2) SAR 值为 2.0~5.0 的中等 SAR 沸石膜；3) SAR 大于 5.0 的高 SAR 沸石膜。低 SAR 沸石膜，如 NaA 和 NaY 是亲水性的有机溶剂脱水膜，但在酸性介质中 Al 原子易从 NaA 框架中分离，最终使得分离性能降低。然而，高 SAR 的膜亲水性差，不利于乙酸/水溶液的分离。因此，中等 SAR 沸石膜在保持较高亲水性的同时仍具有优良的耐酸性能，是制备乙酸渗透汽化脱水膜的首选材料。

在各种沸石骨架中，ZSM-5 通常由锯齿形通道组成，其骨架 SAR 在 2.5 至无穷大的范围内可调，进而调整膜的亲水性和耐酸性，使其在乙酸渗透汽化脱水中有巨大的发展前景。研究表明，随着分子筛膜的孔径增大，膜的亲水性减小，耐酸性增大。因此，必须优化 Si/Al 比以获得酸稳定的 ZSM-5 膜。Li 等[34]在 Al_2O_3 管外表面采用种子辅助结晶法制备了 Si/Al = 11.9 的 ZSM-5 沸石膜，通过碱改性可以选择性的提取其骨架中的 Si 原子而不破坏膜的微观结构，从而使膜的亲水性提高。值得注意的是，沸石膜的制备很大程度上受边界缺陷、活性沸石层厚度和晶粒取向的限制。此外，Al 原子的分布也会对膜的微观结构产生影响。Zara 等人[35]通过调整 ZSM-5 膜层间铝的空间分布从而制备高性能稳定的乙酸脱水膜。该 ZSM-5 膜在较宽的乙酸浓度范围内的水渗透通量为 2.67~1.10 $kg \cdot m^{-2} \cdot h^{-1}$，且具有良好的热稳定性及化学稳定性。最近，Chen 等人[36]报道了通过氟介导的有机无模板凝胶制备富铝 ZSM-5 膜。该研究中报道的致密富铝 ZSM-5 膜在 75℃，90wt%乙酸溶液中，渗透总通量为 0.98 $kg \cdot m^{-2} \cdot h^{-1}$，分离因子为 3200，这进一步说明了通过氟化介质制备的 ZSM-5 膜具有优良的酸稳定性。但是膜脆性大、材料成本高、制备过程复杂等因素阻碍了其商业化应用。

具有较小孔径的 T 型和 CHA 型沸石分子筛的亲水性较强，且耐酸性优良，是乙酸脱水中两种性能突出的材料。Cui 等[37]通过水热合成法制备了 T 型沸石膜，在 75℃，进料液中乙酸含量为 50wt%的条件下，该膜具有优异的分离性能及良好的稳定性。Gu [38]实验室报道了中等 SAR 的 CHA 型沸石膜用于乙酸脱水。该 CHA 膜具有较高的酸稳定性和有最佳的硅铝比，这将为制备用于腐蚀介质中溶剂脱水的高通量膜打开新的大门。Yamanaka 等[39]以苯基三甲基铵阳离子(BTMA+)为导向剂，采用分子筛间转换法在 αAl_2O_3 载体上制备得到 CHA 型分子筛膜。在 75℃、进料液中乙酸为 50wt%时，膜的渗透通量和分离因子分别为 7.80 $kg \cdot m^{-2} \cdot h^{-1}$ 和 2480。近几年，疏水 MFI 型沸石膜渗透汽化分离水溶液中低浓度有机物已有大量报道[40] [41] [42] [43]。从文献中可以清楚地看出，各种类型的无机膜在酸性溶液中有很大的脱水应用潜力。表 2 列出了无机膜分离乙酸和水的 PV 性能。

Table 2. Comparison of PV performance of inorganic membranes for separation acetic/acid mixtures
表 2. 无机膜分离乙酸和水混合物的 PV 性能比较

膜	乙酸/水混合物(wt%)	T(℃)	通量/J ($kg \cdot m^{-2} \cdot h^{-1}$)	分离因子 α	参考文献
ZSM-5	50-50	70	0.785	381	[34]
ZSM-5	90-10	75	0.25	165	[44]
ZSM-5	75-25		0.85	230	
ZSM-5	50-50		2.21	200	
ZSM-5	30-70		2.60	115	
ZSM-5	15-85		3.40	125	

Continued

CHA	50-50	75	8.00	2500	[39]
MOR	90-10	75	0.97	1200	[45]
Zeolite T	50-50	75	0.90	520	[37]
Silicalite-1	98-2	80	0.45	∞	[46]
Silica	50-50	90	5400	125	[47]
Silica	90-10	25	0.016	324	[48]

不同种类的膜由于自身材料的化学性质与物理结构具有不同的优缺点。由于聚合物膜更加经济廉价，并且具有较高的渗透通量和良好的选择性，在渗透汽化分离共沸组成时聚合物膜是最优的选择。但是，无机膜在涉及酸性或碱性溶液的分离时则显现出更优异的稳定性[49]。表 3 列出了有机膜与无机膜分离乙酸和水混合物的优缺点比较。

Table 3. Comparison of advantages and disadvantages between organic membrane and inorganic membrane for separation of acetic acid
表 3. 有机膜与无机膜分离乙酸的优缺点比较

膜	膜材料	优点	缺点
有机膜	纤维素衍生物类、聚砜类、聚酰胺类、聚烯烃类、乙烯类聚合物、含硅聚合物、含氟聚合物等	成本低、种类丰富、操作简单、制备技术成熟	不耐高温、不耐溶剂、易发霉、易溶胀
无机膜	金属、陶瓷、氧化硅、沸石(ZSM-5、A 型、Y 型和 MOR)、MOFs 等	稳定性好、机械强度大、无溶胀	脆性大、材料成本高、制备过程复杂

3. 挑战及展望

提高膜耐酸性的同时获得最佳的分离性能是乙酸脱水的主要挑战。在实际的工业乙酸脱水中，膜材料往往在通量、分离因子和稳定性等方面存在很多权衡限制。尽管沸石膜在酸性条件下有巨大的发展潜力，但其复杂的合成过以及成本高等问题阻碍了沸石膜在工业水平上的应用。因此，研究廉价且机械性能良好的沸膜，将为其在工业中的应用提供经济可行性。

传统的聚合物膜和无机膜在恶劣环境中稳定性较低，不适合用于乙酸脱水。近年来，许多研究人员为了提高膜的稳定性和经济实用性，已经对其进行了许多改性。然而，制备成本、分离性能和膜组件的配置等因素仍然阻碍了乙酸脱水膜在工业水平上的应用。在这方面，中空纤维膜技术因其较高的填充密度和通量而具有广阔的工业应用前景。近年来，渗透汽化膜分离技术在我国取得了巨大的突破和进展，并为绿色环保工艺及节能减排做出了一定的贡献，在未来的发展中将发挥重要作用。

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