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Capillary supported ultrathin homogeneous silicalite-poly(dimethylsiloxane) nanocomposite membrane for bio-butanol recovery

Xinlei Liu [a,b], Yanshuo Li [a], Yi Liu [a,b], Guangqi Zhu [a], Jie Liu [a], Weishen Yang [a,*]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

An ultrathin (300 nm) homogeneous silicalite-poly(dimethylsiloxane) (PDMS) nanocomposite membrane was fabricated on capillary support by a "Packing–filling" method. Firstly, silicalite-1 nano-crystals were deposited onto a porous alumina capillary support using dip-coating technique (packing); secondly, the interspaces among the nano-crystals were filled with PDMS phase (filling). No voids between nano-crystals and PDMS phase were observed by scanning electron microscopy (SEM), suggesting good zeolite–polymer adhesion. The membrane possesses very high flux (5.0–11.2 kg m^{-2} h^{-1}) and good separation factor (25.0–41.6) for the pervaporative recovery of iso-butanol from aqueous solution (0.2–3 wt.%) at 80 °C. Such properties offer great potential towards applications in fermentation–pervaporation coupled processes. The effects of feed temperature and concentration on the pervaporation performance of this nanocomposite membrane were investigated.

1. Introduction

With the increasing global demand for renewable transport fuels, bio-ethanol has become popular today. It is mostly used as blending agent with gasoline (gasohol) to increase octane and cut down carbon monoxide and other smog-causing emissions [1]. Besides ethanol, butanol began to attract people's attention as a next-generation biofuel. Compared with ethanol, butanol possesses many unique advantages, including higher combustion value, lower volatility, and lower freezing point [2]. With the state-of-the-art butanol fermentation technique, the final concentration of butanol in fermentation broths is generally low (normally less than 3 wt.%), mainly because of severe product inhibition and toxicity by butanol. Distillation is a traditional yet very energy intensive recovery option for butanol. Therefore, alternative recovery technologies that can lower the recovery costs, thus improving the bio-butanol economics are highly demanded, such as liquid–liquid extraction, adsorption, gas stripping, steam stripping, and pervaporation [3]. From an energy requirement perspective, pervaporation is considered to be one of the most attractive options [4]. Moreover, membrane pervaporation can be effectively integrated with bioreactor to realize continuous fermentation, which has attracted remarkable interests in the field of biotechnology [5].

Extensive researches had been performed to find optimized hydrophobic pervaporative materials to maximize the separation performance of butanol-selective membranes in items of separation factor, flux, and operating stability [6]. The most intensively studied materials include poly(dimethylsiloxane) (PDMS) [7–10], poly(1-trimethylsilyl-1-propyne) (PTMSP) [11,12], and poly(ether-block-amide) (PEBA) [2,13]. PDMS is an "organic–inorganic" elastomeric material, often referred to as "silicone rubber", exhibiting excellent film-forming ability, thermal stability, chemical and physiological inertness [14]. The rapid chain segment motion in the PDMS leads to a large free volume that favors the diffusion of the permeating molecules. At least for the near term, PDMS will continue to be the benchmark membrane material for hydrophobic pervaporation membrane [6]. The reported butanol–water separation factors for PDMS membranes generally ranged from 15 to 50. However, the total fluxes of these dense PDMS membranes are normally less than 1.0 kg m^{-2} h^{-1} [7,9,15]. Reducing membrane thickness can increase the membrane flux proportionally. However, due to the strong swelling effect of PDMS by hydrophobic alcohol molecules, the membranes become unstable when their thickness was reduced to sub-micron level.

Since the introduction of silicalite-filled PDMS membranes by Te Hennepe et al. [16], remarkable improvements on membrane performance due to incorporation of zeolites have been reported [9,17–19]. Molecular sieving effects [20], hydrophobic/hydrophilic characters [21,22], and the so-called physical cross-linking functions of the zeolites [21,22] have been utilized to increase the selectivities and the stabilities of the composite membranes, also

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* Corresponding author. Tel.: +86 411 84379073; fax: +86 411 84694447.
E-mail address: yangws@dicp.ac.cn (W. Yang).
URL: http://yanggroup.dicp.ac.cn/ (W. Yang).

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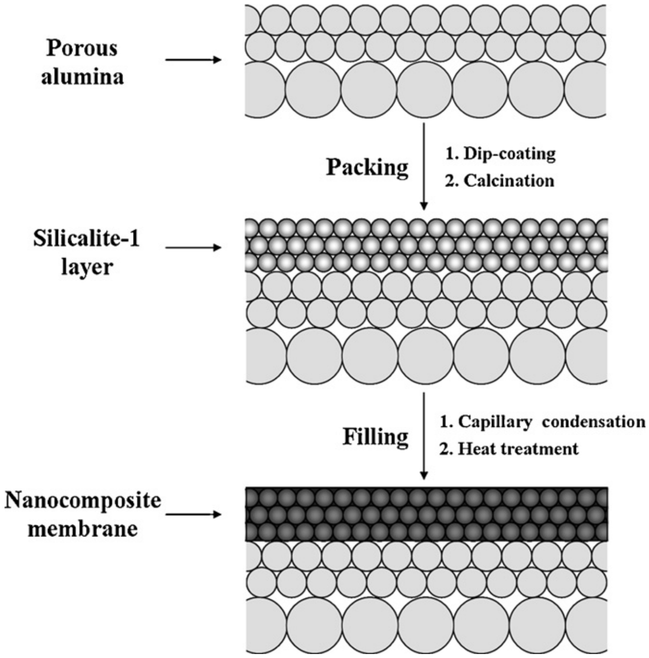

Fig. 1. Schematic illustration of the fabrication procedure of the silicalite-PDMS nanocomposite membrane by a "Packing–filling" method.

named as mixed matrix membranes (MMMs). To date, nevertheless, most of the studies used zeolites with particle sizes in the micron range. As a consequence, the thickness of the composite membranes was inherently high. The development of zeolite nano-crystals provides the opportunity to prepare thin composite membranes. The simplest way to fabricate zeolite–polymer composite membrane is solution blending [23]. However, the tendency of the particle agglomeration is inversely related to the particle size [18] and hence the preparation of high-quality nanocomposite membranes is hampered. Well-known approaches, such as organic functionalization of the fillers (e.g. fumed silica), aiming at matching the polarity of the particle surface groups with the polymer medium, have been developed for a better dispersion of the inorganic phase [24]. Nevertheless, the dispersion of zeolite nano-crystals modified by silane coupling agent in polymer membrane is still non-homogeneous [25]. Furthermore, this procedure for fabricating nanocomposite membranes which includes functionalization of the fillers is relatively complicated. Therefore it is highly desirable to develop a simple and efficient method for fabricating homogeneous nanocomposite membranes.

The kind of supports of pervaporation membranes should also be taken into account. Compared with tubular supports, hollow fibers possess the advantage of very high packing density, but are difficult to seal and the transport resistance is large in the core side. Capillary supports provide a compromise solution, combining high packing density, high mechanical stability and low transport resistance.

In this communication, we combine silicalite-1 nano-crystals and PDMS in a new manner instead of dispersing the zeolite in the polymer directly. The fabrication procedure is schematically illustrated in Fig. 1. Firstly, silicalite-1 nano-crystals were deposited onto a porous alumina capillary support using dip-coating technique. A nano-crystal layer was then enhanced to the support after being calcined. Secondly, the interspaces among the nano-crystals were filled with PDMS phase using capillary condensation effect. Vacuum assisted heat treatment was performed to remove the solvent and facilitate the cross-linking among the PDMS chains and between the silicalite-1 nano-crystals and the PDMS chains. In this way, an ultrathin and very homogeneous silicalite-PDMS active layer was uniformly coated onto the thin-walled capillary. The nanocomposite membrane showed a very high flux for extracting low concentration iso-butanol from water. The effects of feed temperature and concentration on the pervaporation performance of this nanocomposite membrane were investigated.

2. Experimental

2.1. Membrane synthesis

Silicalite-1 nano-crystals were hydrothermally synthesized under relatively mild conditions by a modified recipe [26]. Firstly, 20.0 g of tetrapropylammonium hydroxide (TPAOH, Aldrich, 20 wt.%) was mixed with 2.0 g of deionized (DDI) water under stirring. After formation of a homogenous solution, 11.4 g of tetraethoxysilane (TEOS, Kermel, AR) was added and stirred at room temperature for 24 h. Subsequently, the clear solution was transferred to a Teflon-lined autoclave, heated up to 90 °C and kept for 24 h statically. After hydrothermal synthesis, the product was centrifuged at 15,000 rpm for 1 h and ultrasonically washed with DDI water for another 1 h for 3 cycles. The pH value of the as-prepared silicalite-1 suspensions falls to 8–10.

Alumina capillary supports (from Hyflux Ltd., InoCep® M40. 3.7 mm outside diameter, 2.4 mm inside diameter, 10 cm length, and ca. 40 nm pore size in the top layer) were sonicated for 5 min to remove the impurity physically adsorbed on the surface, then dried in an oven at 50 °C. The outer surface of the support was wrapped with Teflon tape. Silicalite-1 nano-crystals dispersed in DDI water (0.2 wt.%) were sonicated for at least 1 h before dip-coating. 1.0 cm/s dipping speed, 10 s immerging time and 1.4 mm/min withdrawing speed were employed to coat the nano-crystals onto the inner surface of the support at 20 °C. After drying 12 h at 20 °C and another 12 h at 50 °C, the silicalite-1 layer was further calcined to remove templates in the frameworks with a ramp speed of 0.5 °C/min and kept at 500 °C for 2 h.

To prepare silicalite-PDMS nanocomposite membrane, 1.5 g of PDMS (vinyl terminated) and 0.3 g of curing agent (methylhydrogen siloxane) (Sylgard 184, used as received from Dow Corning Co.) were dissolved in 13.5 g of iso-octane (Kermel, AR). Then, the silicalite-1 coated capillaries were dip-coated into this solution (1.0 cm/s dipping speed) for 10 s and withdrawn at a speed of 1.5 cm/s. After drying at 20 °C for 10 min, the dip-coating process for coating the organic phase was repeated. Afterwards, the membrane was dried at room temperature for 24 h, 50 °C for 3 h and then kept at 50 °C for another 19 h under vacuum.

2.2. Membrane characterization and pervaporation experiments

The morphologies of the as-synthesized membranes were studied by scanning electron microscopy (Quanta 200 FEG, FEI Co., 20 kV). The membrane samples were prepared by freeze fraction in liquid nitrogen and sputter coated with gold.

The separation performance of the as-synthesized capillary membranes was evaluated through pervaporation experiment for removing iso-butanol from aqueous solution. The feed mixture (ca. 2.0 L) was kept between 30 and 80 °C at a composition of 0.2–3.0 wt.% iso-butanol. To minimize the boundary layer effect on the membrane surface, the feed flow rate was kept sufficiently high (2.0 L/min). After circling 10 min for stabilization, the pervaporation performance was characterized. The effective membrane area was ca. 7.0 cm^2. The permeation side was kept under vacuum and the permeate was trapped with liquid nitrogen. The permeation flux was measured by weighing the condensed permeate: $J = W/At$, where W refers to the weight of permeate

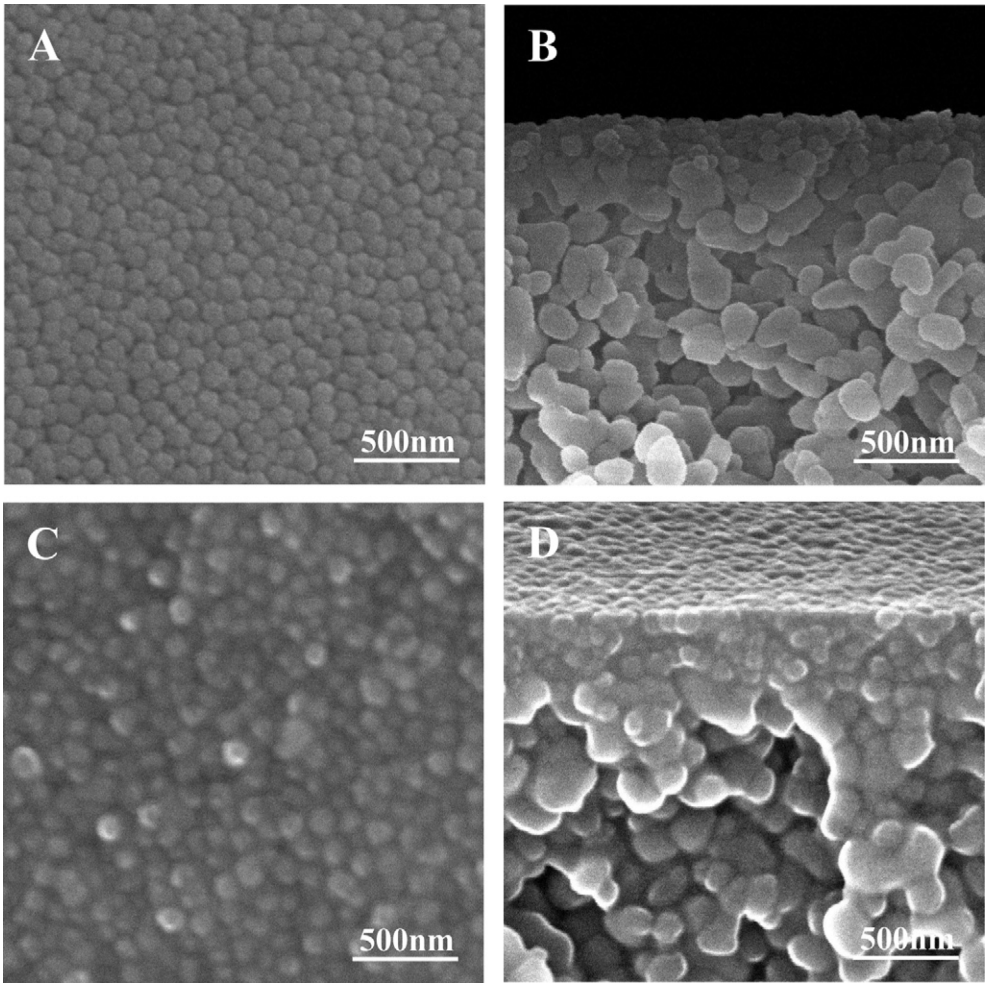

Fig. 2. SEM images: (A) top view and (B) cross section of the dip-coated silicalite-1 nano-crystal layer, (C) top view and (D) cross section of the silicalite-PDMS nanocomposite membrane.

(kg), A the membrane area (m^2), t the duration (h) of the sample collection. The feed and permeate concentrations were measured by an off-line GC (Agilent 7890). The separation factor is defined as $\alpha = (Y_{\text{iso-butanol}}/(1-Y_{\text{iso-butanol}}))/(X_{\text{iso-butanol}}/(1-X_{\text{iso-butanol}}))$, where $X_{\text{iso-butanol}}$ and $Y_{\text{iso-butanol}}$ denote the mass fraction of iso-butanol in the feed and permeate sides, respectively. The pervaporation separation index is defined as $\text{PSI} = J(\alpha - 1)$. In most cases the condensed permeate separated into two phases. In order to measure the concentration of iso-butanol in the condensate, the permeate was diluted with known quantity of water to generate a single phase.

3. Results and discussion

3.1. *Characterization and evaluation of the silicalite-PDMS nanocomposite membrane*

The XRD pattern of the as-synthesized silicalite-1 crystals is in good agreement with the previous report [26]. The average crystal size is about 80 nm. A smooth and crack-free silicalite-1 layer was coated on the inner surface of the alumina capillary support using dip-coating technique (Fig. 2A). Fig. 2B shows that the close-packed silicalite-1 layer is about 300 nm thick. Before filling with PDMS, the templates in the channels of the silicalite-1 nano-crystals were removed by calcining at 500 °C. During the calcination treatment, covalent bonds can be formed among the silicalite-1 nano-crystals and between the silicalite-1 nano-crystals and the support [27]. This rigid assembly of silicalite-1 nano-crystals will act as zeolitic skeleton for the following construction of the silicalite-PDMS nanocomposite membrane.

By dip-coating the silicalite-1 layer with PDMS, the interspaces among the silicalite-1 nano-crystals were completely filled with the polymeric phase. No voids between the nano-crystals and PDMS phase were observed, suggesting a good zeolite–polymer adhesion (Fig. 2C). From the SEM top view, the texture of the preformed silicalite-1 layer is still distinguishable, indicating a very thin layer of PDMS on the zeolite sub-layer. Fig. 2D represents the cross-section image of the nanocomposite membrane. The thickness of the nanocomposite membrane is almost the same as the dip-coated silicalite-1 layer (about 300 nm). The so-obtained nanocomposite membrane possesses very high zeolite loading (74 vol.%), as calculated using closest packing model. This is by far the highest loading rate that can be obtained in terms of homogeneous mixed matrix membranes. Normally, due to the unavoidable aggregation of the fillers (nano-crystals of zeolites), it is difficult to obtain a loading rate higher than 30 vol.% [18]. This ultrathin and high-loading composite membrane offers the possibility to achieve a very high flux for pervaporation separation of butanol without obvious membrane swelling.

Table 1 summarizes the pervaporation performance of the membranes previously reported, as well as our silicalite-PDMS nanocomposite membrane for butanol recovery. The reported separation factors are in the range of 5.2–96.0. The silicalite-PDMS

Table 1
Pervaporation performance for butanol recovery.

Membrane	Feed concentration (wt.%)	Feed temperature (°C)	Total flux (kg m^{-2} h^{-1})	Separation factor	Reference
Ge-ZSM-5	5[a]	30	0.02	19.0	28
PTMSP	2–6[a]	25–37	0.44–0.59	46.3–61.3	11, 12
Surface modified PVDF	7.5[a]	40	2.3	5.2	29
PERVAP-1070	1[a]	70	0.34	47.8	9
Silicalite-PDMS	1[a]	70	0.11–0.61	93.0–96.0	9
PDMS	0.25–5[a]	40–70	0.07–1.0	15.0–50.0	7, 9, 15
PUR	1 [b]	50	0.08	9.2	7
PEBA	1[b]	50	0.24	23.2	7
Silicalite-PDMS	0.2[b]	80	5.0	41.6	This work
	1[b]	80	7.1	32.0	This work
	2[b]	80	8.9	27.6	This work
	3[b]	80	11.2	25.0	This work
			10.0[c]	17.4[c]	This work

[a] *n*-Butanol aqueous solution.
[b] iso-Butanol aqueous solution.
[c] The templates in silicalite-1 were not removed.

membrane reported by Huang [9] possesses the highest separation factor. Ge-ZSM-5 [28], PTMSP [11,12], surface modified poly(vinylidene difluoride) (PVDF) [29], PERVAP-1070 [9], PDMS [7,9,15], poly(urethane) (PUR) [7], PEBA [7] membranes have also been reported for pervaporation separation of butanol–water mixtures. According to the economic appraisal by Vane [3], when butanol–water separation factor is larger than 30, the energy required for pervaporation of butanol will be less than that of distillation. Our silicalite-PDMS nanocomposite membrane meets this target. The total fluxes of reported membranes are normally less than 1.0 kg m^{-2} h^{-1}. The surface modified PVDF membrane shows a high total flux, however, its selectivity is too low to compete with distillation. The fluxes of our membrane are much higher than those of the reported membranes. These fluxes greatly meet the flux requirement of the fermentation–pervaporation coupled processes. The ultrathin and very homogeneous silicalite-PDMS nanocomposite active layer and very low support resistant of the capillary account for this ultrahigh flux.

For comparison, pure PDMS membrane was also prepared by the same procedure on the capillary support. The as-synthesized membrane is about 200 nm in thickness, and showed a high pervaporation flux of 26.1 kg m^{-2} h^{-1} with an iso-butanol–water separation factor of 12.6. However, after being tested for 2 h, this membrane was destroyed due to the swelling induced instability of the PDMS thin layer. From another side, this result indicates that the effects of space restriction and physical cross-linking by the close-packed silicalite-1 nano-crystals play an important role for increasing the membrane stability.

Using the same method but without removal of the templates that occluded in the silicalite-1 nano-crystals, the as-synthesized composite membrane showed a lower separation factor and a lower flux compared with the standard membrane (Table 1). As a consequence, the hydrophobic channels of these silicalite-1 nano-crystals also made a considerable contribution to the selective permeation of iso-butanol molecules.

3.2. Pervaporation performance for iso-butanol recovery

Fig. 3 shows the influence of temperature on pervaporation performance at a feed composition of 3 wt.% iso-butanol. Both water and iso-butanol fluxes increased with temperature, due to the increased diffusion coefficients of the permeating molecules, as well as the increase of desorption rate of iso-butanol in silicalite-1 crystal [30]. Huang [9] found that the separation factor decreased at high temperature (70 °C) because the increase of the diffusivity of water was larger than that of butanol. This might be contributed to the enhanced mobility of PDMS polymer segments, and consequently the increased swelling of the membrane. The separation factor of our membrane increased monotonously with temperature and showed no decline even at 80 °C. This result indicates that the effects of space restriction and physical cross-linking by the close-packed silicalite-1 nano-crystals can enhance the membrane stability against serious swelling at high temperature.

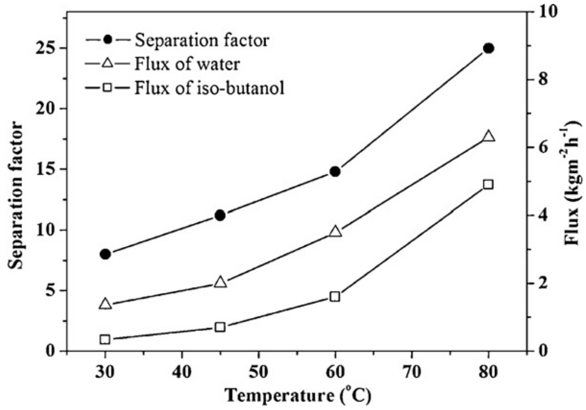

Fig. 3. Effect of feed temperature on pervaporation performance at a feed composition of 3 wt.% iso-butanol.

The influence of feed concentration on pervaporation performance is shown in Fig. 4. The iso-butanol flux increases with feed concentration at the range of 0.2–3 wt.% due to the increased

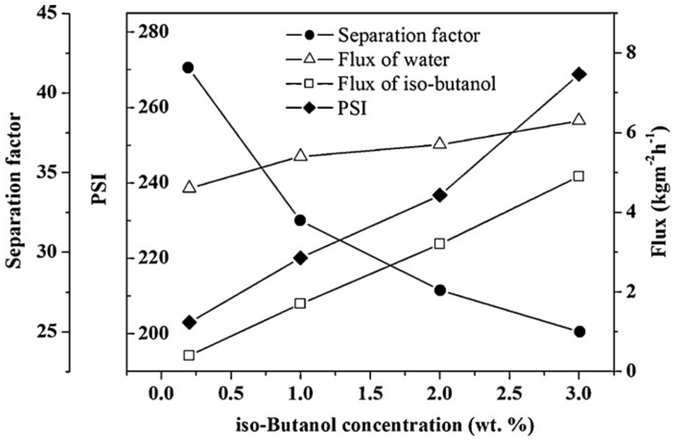

Fig. 4. Effect of feed concentration on pervaporation performance at 80 °C.

sorption amount of iso-butanol in the membrane, and thus the enhanced driving force of iso-butanol component. Simultaneously, the increased sorption of iso-butanol tended to increase the free volume and chain mobility of the polymer. Consequently, the diffusion of water through membrane was enhanced. Furthermore, the coupling effect, originated from hydrogen bonding between water and iso-butanol, resulted in an increase of water flux. The denominator term in the separation factor relationship becomes large at high feed iso-butanol concentrations, thus giving low separation factor. Owing to the tremendous increase of iso-butanol flux, the pervaporation separation index (PSI) increases with feed concentration.

4. Conclusions

A novel method ("Packing–filling") is developed to fabricate ultrathin homogeneous silicalite-PDMS nanocomposite membrane on capillary support. Silicalite-1 nano-crystals were deposited onto porous alumina capillary support, and then, PDMS filled the interspaces among the nano-crystals uniformly. No voids between nano-crystals and PDMS phase were observed, suggesting good zeolite–polymer adhesion. The membrane possesses very high flux (5.0–$11.2\,\mathrm{kg\,m^{-2}\,h^{-1}}$) and good separation factor (25.0–41.6) for the pervaporative recovery of iso-butanol from aqueous solution (0.2–3 wt.%) at 80 °C. The ultrathin (300 nm) and very homogenerous silicalite-PDMS nanocomposite active layer and the very low support resistant of the capillary account for this ultrahigh flux. Such properties offer great potential towards applications in fermentation–pervaporation coupled processes.

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