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Crosslinked MOF-polymer to enhance gas separation of mixed matrix membranes

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ABSTRACT

Preparation of mixed matrix membranes (MMMs) from rigid polymers like PIM-1 remains challenging because the contorted and rigid polymer chains of PIM-1 severely inhibit self-rearrangement leading to low quality of polymer-filler interaction. MMMs prepared by conventional methods, therefore, often suffer from defects at the polymer-filler interface. In this work, a novel filler having hydroxyl functional groups on the surface (Mg-MOF-74) was used as a filler and mixed with PIM-1 in solution (chloroform). Under optimized solution conditions (65 °C and 24 h), chemical crosslinking between the hydroxyl groups and the fluoride chain-ends of PIM-1 was facilitated, to completely remove these interfacial defects. The crosslinked MMMs were then characterized by XRD, FTIR, SEM and mechanical tests, while their separation properties were studied for five gases including H_2, CO_2, CH_4, N_2 and O_2 upon increasing Mg-MOF-74 loading (0–20% wt.). The two main features of MOF-74 (also known as CPO-27), especially Mg-MOF-74, greatly contributing to the membrane gas separation were 1-D hexagonal channels (1.1 nm diameter) and an exceptionally high CO_2 adsorption capacity under reduced pressures. As the ends of PIM-1 are directly linked with the MOF surface, the intrinsic micropores of PIM-1 are connected to the inner pores of MOF-74 forming an inter-connected micropore network throughout the MMM. Both selectivities and permeabilities of MMM were improved for all the gases, particularly CO_2 permeability which increased by 3.2 times from 6500 Barrer for the neat polymer (PIM-1) to 21,000 Barrer for PIM-1 with 20% wt. of MOF-74, meanwhile CO_2/CH_4 selectivity was improved from 12.3 to 19.1, respectively.

1. Introduction

Membrane-based gas separation, due to its smaller footprint and energy efficiency, is emerging as an alternative technique replacing traditional processes in gas purification industry such as nitrogen separation from air, CO_2 removal from bio-gas or natural gas and hydrogen elimination from petrochemical streams [1,2]. Separation performance of polymeric membranes is undeniably limited by the trade-off relationship between permeability (P) and selectivity ($\alpha = P_A/P_B$), known as Robeson upper bounds [3,4]. Recently developed polymer of intrinsic microporosity (PIMs) with rigid and contorted polymer chains, which create micropores leading to exceptionally high permeability and reasonable selectivity close to the trade-off bounds, may be among the most promising materials for gas separation [5,6]. Though still not fully understood, the intrinsic micropores in PIM-1 are believed to be connected with bottle-necked slits (as shown in Scheme 1a). Experimental data for PIM-1 shows that permeability for H_2 (2.89 Å) is considerably lower than that for larger molecules like CO_2 (3.3 Å) [6]. Hence, gas transport in PIM-1 should not be solely driven by micropore-based sieving effects but at least partly by solution-diffusion mechanism [7]. To improve solubility selectivity, post-polymerization is generally used to introduce CO_2-philic moieties including N-containing heterocyclic, hydroxyl or carboxyl groups onto the PIM-1 backbones that can induce Lewis acid – Lewis base interactions with CO_2. Du et al. [8] reported a hydrolysis route to prepare carboxylated PIM-1 membranes with tunable gas transport properties depending on the hydrolysis degree. A CO_2/N_2 ideal selectivity of 26, about 136% higher than for neat PIM-1, with a significant decrease in CO_2 permeability (620 Barrer) was observed. Du et al. [9] also prepared tetrazole-functionalized PIM-1 (TZ-PIM-1) showing impressive separation performance, where mixed gas selectivities for CO_2/N_2 and CO_2/CH_4 were 41 and 22, respectively, without significant loss in CO_2 permeability ($\sim$3000 Barrer). Recently, Swaidan et al. [6] prepared and characterized an amidoxime-functionalized PIM-1 (AO-PIM-1) having

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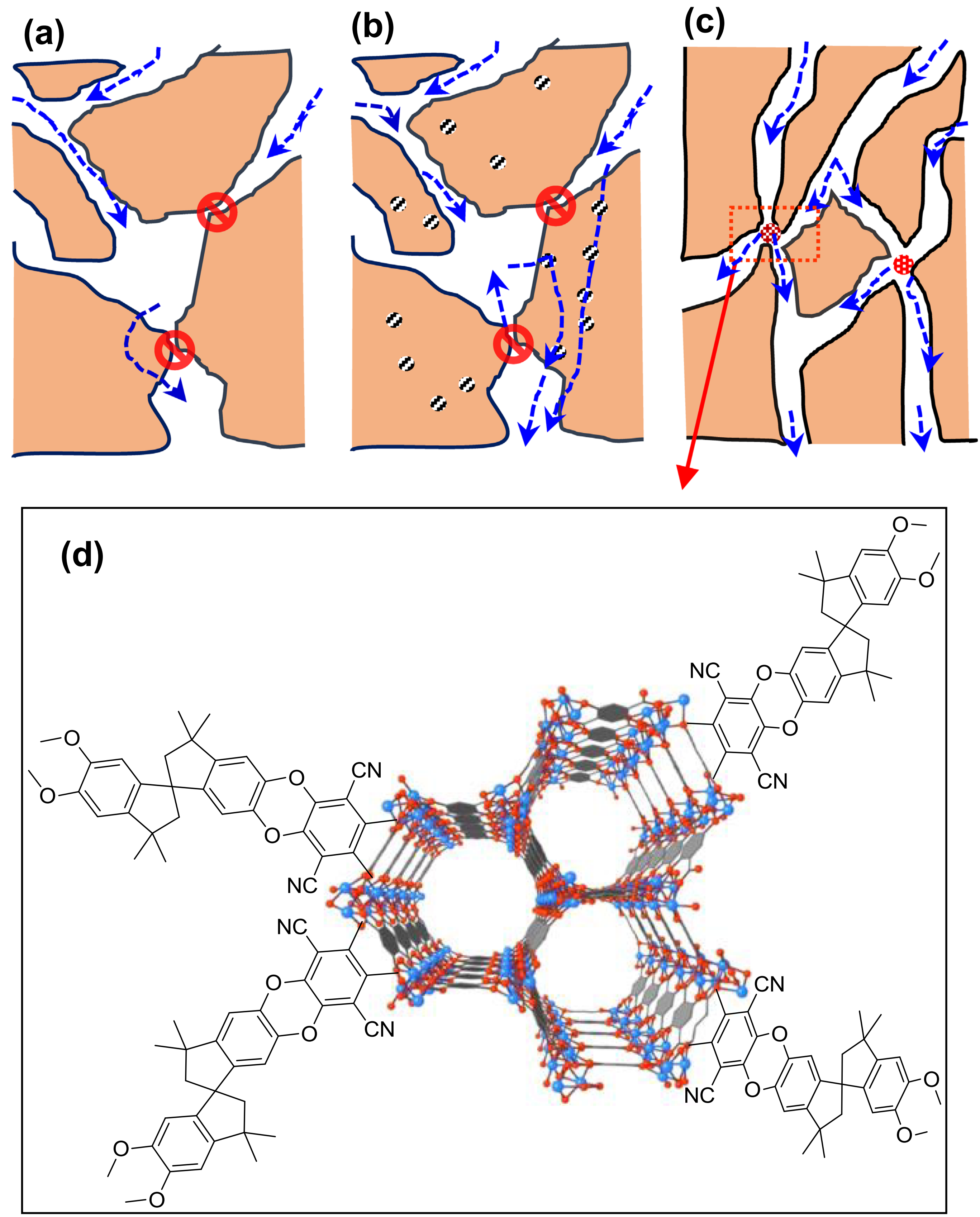

Scheme 1. Illustration of gas transport for: (a) neat PIM-1 showing inter-connected pores with bottle-necked slit, (b) MMMs without polymer-filler cross-link, hatched areas indicate fillers working as secondary pathway to get gas passed the bottle-necked slit, (c) and (d) MMMs with polymer-filler crosslink, inner pores of fillers directly connect with the micropore network of PIM-1, accelerating gas transport.