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Effects of structural crystallinity and defects in microporous Al-MOF filled chitosan mixed matrix membranes for pervaporation of water/ethanol mixtures

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ABSTRACT

A new two-dimensional microporous metal organic framework (MOF), Al-MOF, [Al(OH)(MBA)] (CYCU-7, MBA = diphenylmethane-4,4′-dicarboxylate anion) and its reported analogue, [Al(OH)(SBA)] (CAU-11, SBA = 4,4′-sulfonyldibenzoate anion), have been synthesized using hydrothermal and solvothermal methods, respectively, and their structural crystallinities and defect porosities were carefully controlled and characterized by N_2 sorption isotherms and ^{27}Al solid-state nuclear magnetic resonance measurements. Interestingly, the MOF synthesized by the ethanol-based solvothermal method (CYCU-7) show a significant degree of linker-missing defects compared to that synthesized by the water-based hydrothermal method (CAU-11). We further incorporated the synthesized CYCU-7 and CAU-11 with chitosan (CS) biopolymer to make CYCU-7@CS and CAU-11@CS mixed matrix membranes (MMMs) with the loading amount of MOF 2.5, 5.0, or 10 wt%. The as-prepared CYCU-7@CS and CAU-11@CS MMMs were applied for separation of water/ethanol mixtures through the pervaporation process, and the effects of the structural properties (*e.g.* crystallinity and defects) of CYCU-7 and CAU-11 on the separation performance are studied. It is found that defect-rich CYCU-7@CS MMMs exhibit higher flux, while CAU-11@CS MMMs with higher crystallinity exhibit a higher separation factor. In addition, the CAU-11@CS MMM with 5.0 wt% loading of CAU-11 displays the best separation performance (separation factor = 2741 and flux = 458 g/m^2 h).

1. Introduction

In recent years, metal–organic frameworks (MOFs) have been established as an emerging class of new porous materials that are valuable for energy-related applications such as gas storage [1], catalysis [2–6], and separation [7,8]. Comparatively, MOF materials have advantages for separation applications over conventional inorganic porous materials such as zeolites, because it is possible to control the pore size and surface functionality of MOFs [9,10]. MOFs are coordination polymers consisting of metal ions (or clusters) and organic linkers [9,11]. To tune and limit the pores to a certain size for selective adsorption and separation applications has been a major concern for MOFs [7,12–20]. In this regard, MOFs with two-dimensional (2D) porous structure are in high demand because of their tuneable flexibility and

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interdigitated networks dominated by guest molecules filling in the voids between adjacent layers [18–22]. Despite some pioneering studies [21–24], however, 2D porous MOFs have been relatively less studied.

The development of renewable energy is scientifically important and technologically challenging owing to the shortage of energy around the world. One type of renewable energy is bioethanol, which is usually generated from lignocellulosic biomass conversion. For the production of bioethanol, pervaporation (PV) is widely used to separate water from the bioethanol to increase its concentration. The PV process is a membrane separation process for the dehydration of alcohols. In general, polymeric membranes such as chitosan (CS) and polyvinyl alcohol (PVA) polymers are used in the pervaporation process [8,25,26]. Polymeric membranes do not exhibit high mechanical strength, however, resulting in a high degree of swelling during operation [27–33]. In this regard, inorganic nanoporous materials with high mechanical strength, along with good thermal and chemical stability, have been widely used as additives to polymeric membranes to resolve the swelling problems, and such inorganic nanoparticle-containing polymeric membranes are called mixed matrix membranes (MMMs) [34–38]. Many researchers have demonstrated MMMs that incorporate various kinds of inorganic microporous fillers to effectively increase the separation factor. The flux of MMMs with microporous fillers is usually low, however, due to the large mass transfer resistance from the pore size of micropores in the inorganic fillers [39–41]. In contrast, MMMs that incorporate mesoporous fillers can increase the flux, but their corresponding separation factors would decrease due to the large pore sizes in the fillers [42,43]. Consequently, it is important to develop new filler materials with optimized pore size and particle size. We strongly believe that the 2D MOF materials would be promising candidates, owing to their unique pore configuration.

We have previously synthesized a 2D MOF material using 4,4′-sulfonyldibenzoic acid (H_2SBA) as the linker [22]. For the purpose of pervaporation of ethanol/water, our proposed strategy was to construct 2D Al-containing MOFs using $Al(NO_3)_3{\bullet}9H_2O$ as the metal source and diphenylmethane-4,4′-dicarboxylic acid (H_2MBA) as the linker. The cheaper cost and superior stability of Al-MOFs make them more suitable than other MOFs for industrial applications [44,45]. Based on this consideration, here, we synthesize new 2D microporous Al-MOFs including [Al(OH)(MBA)] (namely, CYCU-7) and its isostructural counterpart [Al(OH)(SBA)] (namely, CAU-11). The CYCU-7 and CAU-11 are isostructural 2D MOFs having layers with lozenge-shaped pores, and the latter was first reported by the Stock group [21]. In this study, the CYCU-7 and CAU-11 are prepared by two different methods (*i.e.* the hydrothermal and solvothermal methods), with the products denoted as CYCU-7(W) (or CAU-11(W)) and CYCU-7(E) (or CAU-11(E)), respectively. We found that, although the CYCU-7 samples synthesized by these two methods exhibit the same structural architectures, CYCU-7(E) and CAU-11(E) showed a higher degree of defects in their structures.

Although 2D MOF materials are well-known for their potential separation applications, to the best of our knowledge, the use of 2D MOFs as fillers in CS-based MMMs for pervaporation of ethanol/water mixtures has not been reported. Here, we focus on the preparation of Al-MOF/CS MMMs and then study the effects of the structural crystallinity and defects of Al-MOF on its performance in ethanol/water pervaporation. The newly developed 2D Al-MOF based MMMs with higher thermal and chemical stability and microporosity show great potential for pervaporation.

2. Results and discussion

2.1. Characterization of the synthesized Al-MOFs (CYCU-7 and CAU-11)

The Al-MOFs can be synthesized in high yields by reacting three moles of $Al(NO_3)_3{\bullet}9H_2O$ with one mole of ligand (H_2MBA or H_2SBA), with water (*i.e.* hydrothermal) or ethanol (*i.e.* solvothermal) as the solvent at 120 °C for 48 h, as shown in Scheme 1. The field-emission scanning electron microscope (FESEM) images in Fig. S1 (Supporting Information) clearly show the crystallized microscale structure for the synthesized Al-MOFs. We further studied the structures with synchrotron powder X-ray diffraction (PXRD), and the details of the structural model and the refinement of CYCU-7 are given in the Supporting Information. In the structure of both Al-MOFs, the central metal, the Al(III) ion, is hexacoordinated (AlO_6), so that the Al is coordinated to four oxygen atoms from carboxylic acid groups belonging to the linker (MBA or SBA), while the other two coordinated oxygen atoms are of the bridged hydroxide group (μ-OH), as shown in Figs. S2b and S3a (Supporting Information).

The Al-O bond distances range from 1.8201 to 1.9103 Å for CYCU-7 and 1.8481 to 1.9099 Å for CAU-11, which are consistent with earlier reports [21,46]. As reported in many Al-MOF studies, the secondary building unit (SBU) is formed in such a way that the μ-OH groups are bridging the adjacent AlO_6 polyhedra to form chains consisting of trans corner-sharing AlO_6 polyhedra, as shown in Figs. S2c and S3b (Supporting Information) [21]. These SBUs are linked together by the H_2MBA or H_2SDBA linkers in two directions and then generate the 2D layers, which are stacked along the *c*-axis to form the 2D framework structure, as shown in Fig. 1. The rhombus-shaped channels, having window area of 10.70 × 8.67 $Å^2$ (Fig. S2d, Supporting Information) and 10.69 × 9.18 $Å^2$ (Fig. S3c, Supporting Information), respectively, without considering the van der Waals radii of atoms for CYCU-7 and CAU-11, are formed because of the interconnection of SBUs along the *a*-axis through the carboxylate groups of the linker molecules. Since the methylene group is present instead of the sulfone group, there are no interlayer hydrogen bonding possibilities in CYCU-7. In CAU-11, the sulfone groups are pointed toward neighboring SBUs, and the μ-OH groups are aligned along the *c*-axis pointing toward the SO_2 groups.

The PXRD patterns of the as-synthesized Al-MOFs (*i.e.* CYCU-7(W) and CAU-11(W)) exhibit peaks that correspond to guest molecules such as water and free ligands that are present in the pores (Fig. S4, Supporting Information). The presence of guest molecules in CYCU-7(W) and CAU-11(W) was further confirmed by thermogravimetric (TG) analysis (Fig. S5, Supporting Information) and varied temperature (VT) PXRD measurements (Fig. S6, Supporting Information). The TG analysis and VT-PXRD measurements confirm that the hydrothermally-synthesized MOFs, CYCU-7(W) and CAU-11(W), are stable up to 450 °C. Hence, the as-synthesized samples of CYCU-7(W) and CAU-11(W) were activated at 350 °C and 400 °C, respectively, for 2 h to remove the guest molecules from the pores of the frameworks. On the other hand, the as-synthesized samples of CYCU-7(E) and CAU-11(E) were both activated only at 120 °C for 24 h. The TG curves of as-synthesized CYCU-7(E) and CAU-11(E) are also similar to those of their activated counterparts, indicating high thermal stability (Fig. S7, Supporting Information). Furthermore, the PXRD patterns of the as-synthesized samples of CYCU-7(E) and CAU-11(E) mostly match well with the PXRD patterns of their activated counterparts (Fig. S8, Supporting Information). The PXRD patterns of the activated

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