MOFS GROWN WITHIN THE HIGH-INTERNAL EMULSION POLYMER SUPPORT: NEW ADSORBENTS FOR CO$_2$ CAPTURE

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ABSTRACT

This study focuses on the innovative hybridization of Metal-Organic Frameworks (MOFs) and polyHIPEs (polymerized high internal phase emulsion), leveraging their respective porosity at different length scales. By combining Pickering HIPE polymerization and secondary recrystallization at the metal oxide-polymer interface, the study successfully shapes MOF-74 isostructures within polyHIPEs' macropores, creating highly-porous, co-continuous composite monoliths with pronounced macro-microporosity. These composites exhibit superior CO$_2$ capture performance compared to parent MOF-74 powders, with faster adsorption and desorption kinetics, enhanced regeneration capability, and improved CO$_2$ uptake under working conditions.

Keywords: MOF/polymer composite, CO$_2$ capture, gas separation

INTRODUCTION

The urgency to mitigate CO$_2$ emissions has spurred the development of Carbon Capture Storage and Utilization (CCSU) technologies. Solid adsorbents offer a promising alternative to conventional methods like amine scrubbing due to their lower energy requirements for CO$_2$ desorption and also reduced environmental risks.[1] Among these, Metal-Organic Frameworks (MOFs) have garnered significant attention for CCSU applications, due to their tunable properties.[2-3] However, their limited form factor as powders hampers industrial application. Shaping MOF powders into macrostructures is a crucial step forward. Integrating MOFs with mechanically robust polymers to form composite materials addresses these challenges. We introduce a synthetic strategy combining Pickering emulsion-templating and secondary recrystallization to fabricate hierarchical porous MOF-polymer composites.[4] Emulsion-templating, utilizing high internal phase emulsions (HIPEs), has emerged as a technique to create macroporous polymer matrices known as polyHIPEs (PHs). Composites, derived from metal oxide-stabilized HIPEs, show promise, but limitations such as micropore clogging persist.[5] Our approach involves seeding metal oxide (MO) nanoparticles within PH macrostructures to enhance MOF loading and micropore accessibility. Through this method, we successfully fabricate co-continuous MOF 74-PH composites, where microporous MOF-74 phases uniformly integrate within a PH macrostructure, forming an architectural hierarchy. We utilize a poly(dicyclopentadiene) (PDCPD) PH matrix due to its advantageous mechanical properties and the MOF-74 prototype for its high CO$_2$ uptake capacity and valuate the porous properties and CO$_2$ capture performance of MOF 74-based PH composites.

EXPERIMENTAL

PH composites containing metal-oxides were prepared by Pickering HIPE-templating. Water-in-oil (W/O) HIPEs were prepared from a mixture of DCPD monomer (1.30 g), Pluronic® L121 (0.065 g), toluene (50µL) and oleinic acid-coated MO nanoparticles (30 wt% according to the DCPD) in a 3-neck round-bottomed flask equipped with a mechanical stirrer and a dropping funnel. The mixture was stirred at 400 rpm for 5 min and upon continuous stirring at 25°C deionized water (5.5 mL) was added drop-wise. Afterwards, the initiator M2 (1.3 mg) in

toluene (0.25 mL) was added and the emulsion was stirred for further 5 min. Subsequently, the emulsion was transferred to an appropriate mould and cured at 80 °C for 4 h. The obtained monoliths were purified by Soxhlet extraction with acetone for 24 h and subsequently dried in a desiccator under vacuum until the weight was constant.

For recrystallization of metal oxide-based PHs were immersed in a suitable solvent (typically DMF/MeOH) containing 0.05 g of dihydroxyterephthalic acid. The reaction mixture was then heated in an autoclave at 150 °C for 48 hours. After solvothermal treatment, the recrystallized composites were rinsed with acetone and dried at ambient conditions.

RESULTS AND DISCUSSION

Structural properties. HIPEs with 20 wt% of different metal-oxide contents were prepared. The transformations of PH-embedded metal oxide nanoparticles to MOF-74@PH composites seems to be completed in all cases (Figure 1). SEM imaging indicates even distribution of metal-oxide nanoparticles on the polymeric walls in all cases of MO@PH precursors which are recrystallized to MOF-74@PH monoliths. TG analysis was performed to gain additional information about the MOF content within the composites (Table 1). The initial loadings of metal-oxide precursors within the polyHIPE matrices are between 16 and 18 wt.% whereas MOF loadings after recrystallization are in the range between 23 and 25 wt.%.
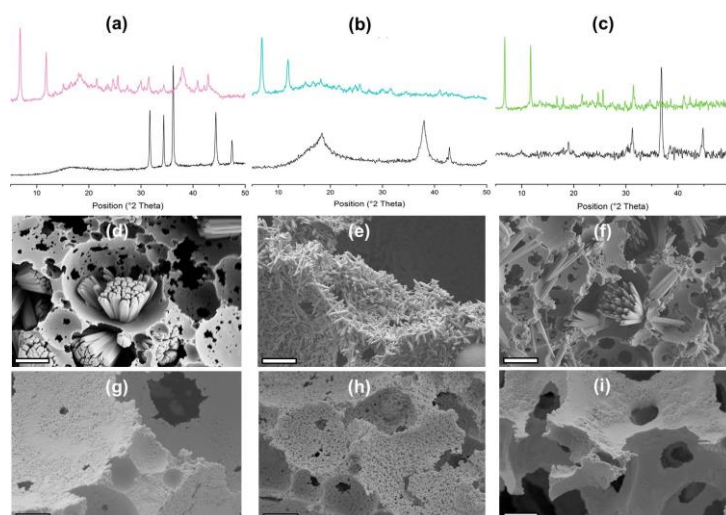

Figure 1. XRD patterns of (a) Zn-MOF-74@PH, (b) Mg-MOF-74@PH and (c) Co-MOF-74@PH composite materials compared with the corresponding MO@PH precursors (black lines); SEM micrographs of (d) Zn-MOF-74@PH, (e) Mg-MOF-74@PH, (f) Co-MOF-74@PH, (g) ZnO@PH, (h) MgO@PH and (i) Co_3O_4@PH composite materials. Scale bar is 1 μm.

Table 1: Metal oxide and MOF-74 loadings within the polyHIPE matrices with oxide to MOF the recrystallization yields based on the TG data.

type of metal oxide and corresponding MOF-74 isostructure	metal oxide loading in MO@PH (wt. %)	MOF-74 content in MOF74@HP (wt.%)	recrystallization yield[1] (%)
Zn	18	23	74
Mg	16	24	55
Co	17	25	77

[1]MOF-74 recrystallization yields from MO@polyHIPE precursors.

Gas accessibilities of MOF-74 micropores were evaluated by N_2 sorption isothermal analysis of the MOF-74@PH composites and the pristine powdered MOF-74 taking into account the loading of MOF phases within the polymer support. MOF-74 powders (Figure 2a) indicate type I isotherms with S_{BET} specific surface areas of 1231 m^2/g, 1264 m^2/g and 1080 m^2/g for

Zn-MOF-74, Mg-MOF-74 and Co-MOF-74 respectively. Monolithic composites on the other hand show BET surface areas with approximately 20% of the values measured for the parent MOFs (245 m^2/g, 257 m^2/g and 198 m^2/g for Zn-MOF74@PH, Mg-MOF74@PH and CoMOF74@PH respectively). The drop of surface area goes mainly on the expense of the presence of poylHIPE matrix which exhibits negligible microporosity. The accessible microporosity of the embedded MOFs which can be estimated by calculations of their surface areas excluding polymer matrix are between 15% and 25 % lower compared to the measured referenced powders taking in account their loadings within PH matrices (Figure 2b).
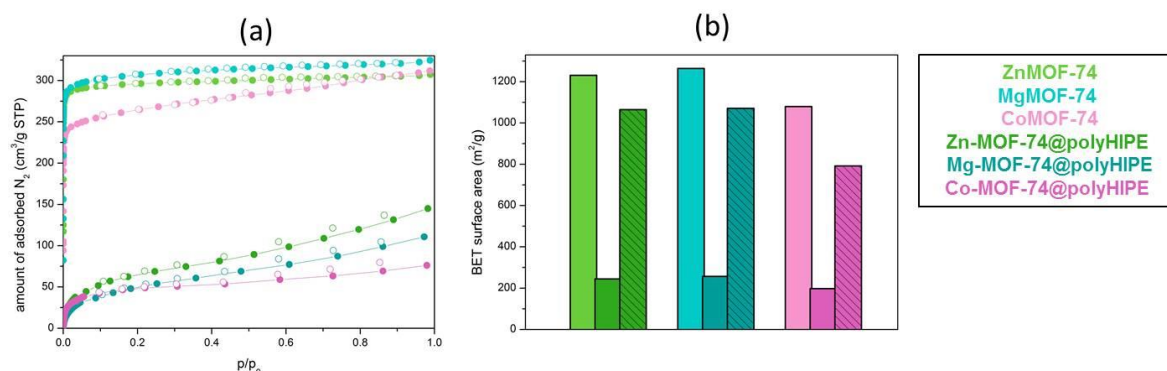

Figure 2: (a) N$_2$ isotherms of MOF-74 powders and MOF-74@PH composites (adsorption points – full symbols, desorption points – empty symbols); (b) BET surface area values for MOF-74 powders and MOF-74@PH composites. Patterned columns show calculated surface areas of pure MOF-74 within the composites, based on the MOF content in PH matrices.

CO$_2$ capture performances. CO$_2$ isotherms measured at 25 °C are shown on Figure 3a. Adsorption capacities of pristine MOF-74 powders are within the expected values (5.2 mmol/g, 8.4 mmol/g and 6.3 mmol/g for ZnMOF-74, MgMOF-74 and CoMOF-74 respectively). CO$_2$ uptakes of composite monoliths are on the other hand within the range between 1.3 and 2.2 mmol/g. Adsorption kinetics of the investigated materials was monitored with CO$_2$ dosing from vacuum to 1 bar at 25 °C (Figure 3b). In all cases, composite monolithic materials exhibit faster adsorption in comparison to the corresponding pristine MOF-74 powders, particular at pre-equilibrium stages. Highly opened macroporous nature of the polyHIPE matrix, MOF-74 crystallites grown from immobilized metal-oxide nanoparticle precursors preventing MOF's substantial agglomeration and significantly lower dimensions of MOF particles within the composites compared to the pristine MOF products together contribute to fast and unobstructed diffusion of CO$_2$ within the microporous channels of MOF-74 framework.
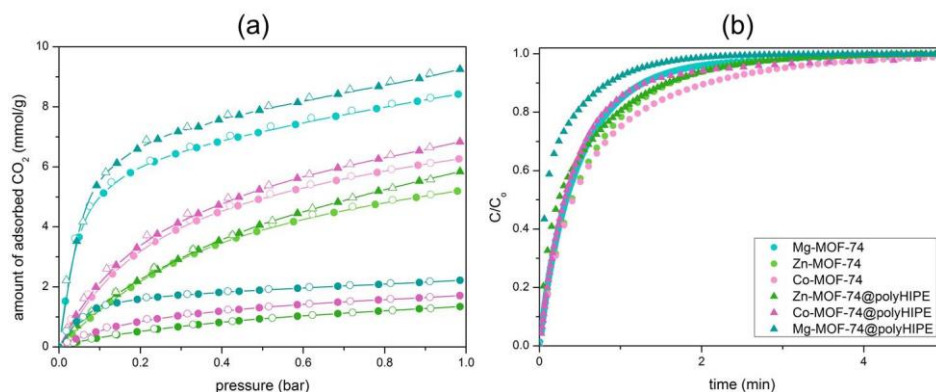

Figure 3: (a) CO$_2$ isotherms of MOF-74 powders and MOF-74@PHs. Circles indicate measured points, whereas triangles represent recalculated values of the pure MOF-74 within MOF-74@PHs based on the MOF content in PH matrices (adsorption points – full symbols, desorption points – empty symbols); (b) adsorption kinetics for MOF-74 powders and MOF-74@PHs.

Investigated products were tested for regeneration process via temperature swing adsorption (TSA) (Figure 4a). Kinetics of CO_2 desorption was followed during the controlled heating using ramp of 5 °C/min. Co-MOF-74, Mg-MOF-74 and Zn-MOF-74 powders release 74.7%, 75.5% and 84.6% of adsorbed CO_2 respectively, when heated up to 150 °C. The regeneration processes are significantly enhanced for Mg-MOF-74@PH and Co-MOF-74@PH releasing 84.2% and 88.0% of captured CO_2 respectively. Due to the more efficient regeneration in the case of MOF-74@polyHIPE composites, working capacities of the composites are expectantly higher in all composite monolithic materials in comparison with the MOF-74 powder analogues.
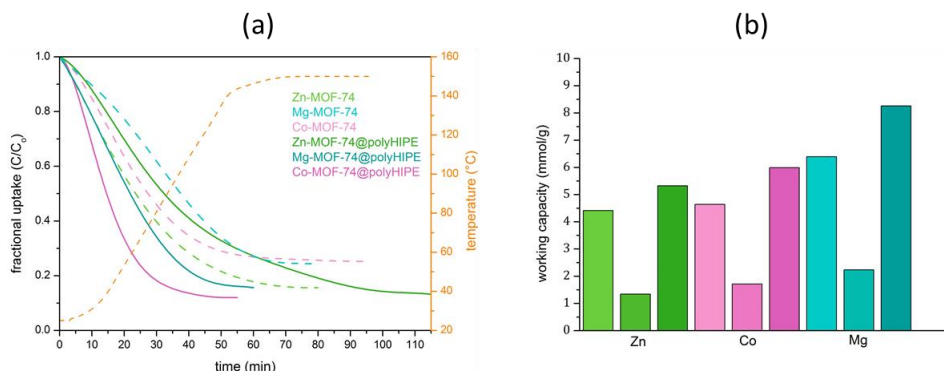

Figure 4: (a) Desorption of CO_2 from investigated materials during heating; (b) working capacities for investigated materials – left pure MOs, middle – composites, right – values normalized to the MOF contribution within the composites.

4. Conclusions

Different MOF-74 isostructures were successfully shaped into polyHIPE matrix using secondary recrystallization approach from the ZnO, MgO and Co_3O_4 nanoparticles embedded within the polymer support. Highly interconnected macroporous structure of the polymer support enables unobstructed diffusion of DHBDC ligand to react with immobilized metal oxide nanoparticles resulting in high recrystallization yields (from 55 % to 77 %) and high accessibility of the MOF's micropores for hosting gas molecules (75 – 85%). The obtained macrostructures with specific hierarchical porosity demonstrate improvement of CO_2 capture performances in comparison to the referenced powdered MOF-74 analogues due to the cooperative adsorption role of active phase and the matrix.

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