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Editorial

Advancements in MOF-Based Engineered Materials for Efficient Separation Processes

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Separation and purification play a crucial role in the production of highly valuable chemical feedstocks in the petrochemical industry. These critical processes involve a range of techniques that are used to isolate and remove impurities, ensuring that the feedstocks meet the necessary quality and purity standards for efficient and effective production. However, traditional techniques such as cryogenic distillation, absorption, and solvent extraction are either ecologically hazardous or energy intensive. In contrast, cutting-edge adsorptive separation technologies based on metal–organic frameworks (MOFs) and their composite membrane materials are more environmentally friendly and energy efficient than conventional distillation and have been extensively utilized to debottleneck separation trains. These new technologies rely on solid porous media known as permeable membranes, which are typically composed of porous materials with nanosized voids.

Adsorption processes that utilize membrane and porous materials rely on three primary mechanisms to enable molecular separation: equilibrium, kinetics, and a synergistic combination of both. In most cases, the equilibrium process dominates and is determined by the difference in thermodynamic affinity, which can be enhanced by modifying the surface of the pores with strong binding sites. Kinetic separation, on the other hand, differentiates between components using the diffusivity difference, which is governed by pore size, rather than using the components' equilibrium loading amounts. Thus, kinetic separation can be improved by fine-tuning the pore size. Some separation processes require a combination of both equilibrium and kinetic mechanisms, necessitating a coordinated control of the interior of adsorbents. To address this challenge, experts from around the world have been invited to contribute articles on this topic, which explore innovative approaches for promoting the development and application of separation processes.

Gas separation is a topic of great interest in the field of separation engineering. Prof. Li's group at Rutgers University is a leading research group in the atomic-level precision design of MOF adsorbents. In this special issue, Prof. Li and coworkers present an effective strategy for improving the uptake of C_2H_6 and C_3H_8 at low pressure by configuring a highly polar surface and suitable pore size. This design concept has led to the successful synthesis of two highly stable Al-based MOFs, MOF-303 and Matériaux de l'Institut Lavoisier (MIL)-160, which demonstrate efficient separation and recovery of C_2H_6 and C_3H_8 from natural gas. The preferential binding of the C–H bond in hydrocarbons to polar atoms or functional groups through hydrogen bonds generates a significant difference in thermodynamic affinity between C_3H_8 (or C_2H_6) molecules and MOFs, thus boosting selectivity for C_3H_8/CH_4 and C_2H_6/CH_4.

Another important means of gas separation is kinetic adsorption separation, which exploits differences in the diffusion behavior of different adsorbates in materials and enables the selection of faster over slower components. Prof. Bao and coworkers present a study on a guest solvent-directed strategy for fine-tuning the pore size at a sub-angstrom precision to realize highly efficient kinetic separation. The resultant CuFMOF·CH_3OH (denoted as CuFMOF-c) from this study exhibits an excellent CO_2/CH_4 kinetic separation performance thanks to a periodically expanding and contracting aperture with the ideal bottleneck size, which enables the effective trapping of CO_2 and impedes the diffusion of CH_4, offering an ultrahigh kinetic selectivity and equilibrium-kinetic combined selectivity. This work not only offers a strategy for fine-tuning the host structure but also indicates that an appropriate pore size is a critical step in efficient kinetic separation, providing important clues for the kinetic separation of other gas mixtures with close size and structural similarity.

In early studies using polymer membranes, separation was achieved through a single-diffusion mechanism, which had a well-known problem of achieving high permeability at the cost of decreased selectivity and vice versa. Mixed-matrix membranes (MMMs) combine porous materials with a polymeric matrix to mitigate these issues and achieve equilibrium-kinetic combined selectivity. The tailorability and diversity of porous materials grant MMMs extendable functionalities and outstanding separation performance in gas separation. In this issue, Prof. Zhao and colleagues review various strategies for rationally matching

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porous materials (including MOFs and discrete metal–organic cages (MOCs)) with polymeric matrices to improve interfacial morphology and gas separation performance; examples include adjusting the geometry and functionality of porous fillers and building connections between fillers and the polymeric matrix through electrostatic, hydrogen, coordination, or covalent bonds. These strategies provide a blueprint for MMM fabrication and reformation in material design and selection.

Separating water-in-oil emulsions is a crucial issue in industrial separation processes, and traditional membrane demulsification technologies require a relatively high transmembrane pressure (> 0.5 bar (1 bar = 10^5 Pa)). Here, Prof. Meng's group and collaborators introduce a new design: an advanced demulsifying MOF-based membrane that uses contact demulsification to quickly and naturally disrupt the water–oil interface balance. The design uses superhydrophobic ZIF-8@rGO@PDMS/PTFE (ZGPP) membranes with a unique micro-nano hierarchical grooved structure to achieve a strong critical surface tension of the water/solid interface, resulting in high oil flux and excellent separation efficiency for oil/water.

This special issue highlights efforts to explore novel MOF-based engineered materials in adsorption/membrane separation processes to overcome challenges in traditional energy-intensive separation technologies. The authors hope that this publication will promote innovation and transformation in the field of separation engineering.