

Composite Hollow Fiber Membrane Reactor Containing Immobilized Organocatalysts and Palladium for Sustainable Chemical Transformation

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Abstract:

Catalytically active asymmetric membranes were developed by crosslinking a polydimethylsiloxane (PDMS) thin layer onto a porous polyamide-imide hollow fiber (PAIHF) support, followed by grafting of aminosilane with hydroxyl derived-PDMS/PAIHF, and finally palladium nanoparticles (PdNPs) immobilization using salicylic aldehyde. Aminosilane and salicylic aldehyde linkers were used to permanently immobilize PdNPs onto the PDMS surface through metal coordination chelation, which prevented their agglomeration and leaching from the catalytic membrane reactor (CMR) module. The obtained CMRs were used as a heterogeneous catalyst and continuous-flow membrane reactor for hydrogenation of 4-nitrophenol, aldol and nitroaldol condensation, Heck coupling, CO₂ cycloaddition and hydroxyalkylation of aniline, and tandem reactions of glucose and fructose to 5-hydroxymethylfurfural (HMF). Our findings also revealed that the turnover frequency (TOF) and selectivity can be tuned and controlled by adjusting the chemistry and degree of cross-linkers, reaction solvents, and flow rates. Even though our polymeric hollow fiber microreactors showed relatively good performance at temperatures up to 150 °C, some amount of active species (e.g., Pd nanoparticles) leached out from the microreactor due to polymer swelling, plasticization, and pore shrinkage during flow reaction, especially when exposed to polar aprotic solvents and aromatics, and deteriorated the stability of the immobilized catalysts.

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