Marrying Organic-Inorganic Hybrid Materials with Polymeric Hollow Fibers for Applications in Catalysis and Adsorptive Separations

Christopher W. Jones* School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA cjones@chbe.gatech.edu

Organic-inorganic hybrid materials based on porous oxide particles functionalized with organic or organometallic moieties enables the tailoring of functional composites for a variety of applications. My group develops such materials for applications in catalysis and adsorptive separations. However, for both commodity and specialty applications, these materials have to be married with suitable gas-solid or liquid-solid contactors to develop truly scalable processes.

In this regard, for the past five years, in collaboration with Koros and Lively at Georgia Tech, we have exploited polymeric hollow fibers as contactors. In this presentation, I will describe the marriage between functional organic-inorganic composite materials¹⁻⁵ with polymeric hollow fibers for large scale CO₂ capture,⁶⁻⁹ enabling CO₂ capture, utilization and storage (CCUS), as well as the first use of composite fibers in low temperature, liquid phase enantioselective catalysis. In particular, this latter part of the talk will describe work done in the NSF Center for Selective C-H Functionalization (CCHF) in collaboration with Davies at Emory University, employing dirhodium carbene catalysts for C-H functionalization and cyclopropanation.¹⁰⁻¹¹

Overall, this work combines sophisticated materials chemistry as well as process knowhow to enable new approaches to catalysis and separations.

1. "Designing Adsorbents for CO₂ Capture From Flue Gas - Hyperbranched Aminosilicas Capable of Capturing CO₂ Reversibly." J.

2. "Dramatic Enhancement of CO2 Uptake by Poly(ethyleneimine) Using Zirconosilicate Supports." Y. Kuwahara et al., *J. Am. Chem. Soc.* **2012**, *134*, 10757-10760.

4. "Important Roles of Enthalpic and Entropic Contributions to CO₂ Capture from Simulated Flue Gas and Ambient Air using Mesoporous Silica Grafted Amines." M. Alkhabbaz et al., *J. Am. Chem. Soc.* **2014**, *136*, 13170-13173.

5. "Linking CO₂ Sorption Performance to Polymer Morphology in Amino-polymer/Silica Composites through Neutron Scattering." A. Holewinski, M. A. Sakwa-Novak, C. W. Jones, *J. Am. Chem. Soc.* **2015**, DOI: 10.1021/jacs.5b06823..

6. "Post-Spinning Infusion of Poly(ethyleneimine) into Polymer/Silica Hollow Fiber Sorbents for Carbon Dioxide Capture." Y. Labreche, R. P. Lively, F. Rezaei, G. Chen, C. W. Jones, W. J. Koros, *Chem. Eng. J.* **2013**, *221*, 166-175.

7. Evaluation of CO₂ Adsorption Dynamics of Polymer/Silica Supported Poly(ethylenimine) Hollow Fiber Sorbents in Rapid Temperature Swing Adsorption." Y. F. Fan et al. *Int. J. Greenh. Gas Control* **2014**, *21*, 61-71.

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C. Hicks, J. Drese, D. J. Fauth, M. Gray, G. G. Qi and C. W. Jones, J. Am. Chem. Soc. 2008, 130, 2902-2903.

^{3. &}quot;Tuning Cooperativity by Controlling the Linker Length of Silica-Supported Amines in Catalysis and CO₂ Capture." N. A. Brunelli, S. A. Didas, K. Venkatasubbaiah, C. W. Jones, *J. Am. Chem. Soc.* **2012**, *134*, 13950-13953.

^{8. &}quot;Dynamic CO₂ Adsorption Performance of Internally Cooled Silica Supported Poly(ethylenimine) Hollow Fiber Sorbents." Y. Fan,

^{9. &}quot;CO₂ Sorption Performance of Composite Polymer/Aminosilica Hollow Fiber Sorbents: An Experimental and Modeling Study." Y. Fan et al., *Ind. Eng. Chem. Res.*, **2015**, *54*, 1783-1795.

^{10. &}quot;Silica-Immobilized Chiral Dirhodium(II) Catalyst for Enantioselective Carbenoid Reactions." K. Chepiga, Y. Feng, N. A. Brunelli, C. W. Jones, H. M. L. Davies, Org. Lett. 2013, 15, 6136-6139.

^{11.} Composite Polymer/Oxide Hollow Fiber Contactors: Versatile and Scalable Flow Reactors for Heterogeneous Catalytic Reactions in Organic Synthesis." E. G. Moschetta et al. *Angew. Chem. Int. Ed.* **2015**, *54*, 6470-6474.