Other - EPIC (Enabling Process Innovation through Computation) Seminar Series

Process Intensification with Near-Critical Media

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Abstract:

The sustainable development/growth of the global chemical enterprise requires technologies that promote process intensification at mild conditions, waste minimization and inherent safety. Over the last two decades, we have rationally exploited near-critical media to develop catalytic technologies that admit these attributes. With relatively moderate pressure changes, it is possible with near-critical media to “tune in” unique combinations of fluid properties (liquid-like density and gas-like transport) that are ideal for enhancing gas/liquid solubility and alleviating mass transfer limitations in multiphase catalysis. Based on complementary modeling and experimental investigations, we have shown how the “effectiveness factor” of mesoporous catalysts (employed in isomerizations, Fischer- Trøpsch synthesis and alkylations) can be maximized by pressure-tuning with near-critical media.

We have also exploited the so-called gas-expanded liquids (GXLs), generated with near-critical gases, in catalysis. At ambient temperatures, gases such as CO2 and light olefins are close to their critical temperatures such that, when compressed to few tens of bars, they dissolve in most conventional solvents creating a continuum of GXLs with pressure-tunable properties. Unlike conventional solvents, GXLs possess free volume that can accommodate permanent gases such as O2, H2 and CO in unusually high concentrations exceeding those governed by Henry’s law. We have harnessed such unique features to address grand challenges in industrial chemistry. Major breakthroughs will be highlighted.

In the first example, we demonstrate total epoxidation selectivity (with no substrate/product burning to CO2!) when near-critical ethylene is oxidized by H2O2 with Re- or Nb-based catalysts at ambient temperatures. The second example involves Rh catalyzed hydroformylation of long-chain olefins with virtually no Rh loss. By dissolving CO2 in the reaction mixture to create a CO2- expanded liquid (CXL), we discovered that the H2/CO ratio in the CXL phase can be optimally pressure-tuned to obtain unprecedented yields of the desired linear aldehyde. Using a soluble polymer to attach the Rh complex, near-quantitative retention of the Rh complex was achieved with a nanofiltration membrane fitted within the stirred reactor. The third example deals with a spray reactor to make polymer-grade terephthalic acid (TPA). Conventional stirred reactor suffers from O2 starvation in the liquid phase resulting in a “crude TPA” that must be purified in a cost-intensive hydrogenation step. In the spray reactor, the liquid phase is finely dispersed in air to enhance gas- liquid interfacial area, resulting in nearly complete p-xylene oxidation to polymer-grade TPA in one step!

Techno-economic analysis and life cycle assessment of these resource-efficient processes reveal that they not only significantly lessen environmental burden (notably greenhouse gas emissions) but are also economically viable. The versatility of these technologies for making products from plant- based feedstocks, including renewable plastic precursors such as 2,5-furandicarboxylic acid (via spray oxidation of 5-hydroxymethylfurfural) and 1,4-butanediol (via hydroformylation of allyl alcohol) will also be highlighted.

Watch the seminar online at: http://lsu.webex.com/meet/nandakumar

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Speaker's Bio:

Bala Subramaniam is the Dan F. Servey Distinguished Professor of Chemical Engineering at the University of Kansas (KU). Subramaniam earned a B.S. in Chemical Engineering from the University of Madras, India and his Ph. D. in Chemical Engineering from the University of Notre Dame. He has also held visiting professorships at the University of Nottingham, United Kingdom and the Institute of Process Engineering, ETH, Zürich, Switzerland.

Subramaniam’s research interests are in catalysis, reaction engineering and crystallization. In particular, his research harnesses the pressure-tunable physicochemical properties of unconventional solvents such as supercritical fluids and gas-expanded liquids in multiphase catalysis to develop resource-efficient technologies with reduced environmental footprint. He has 160+ publications, 27 issued patents and edited 2 books. Subramaniam is the founding Director of the Center for Environmentally Beneficial Catalysis (CEBC), a unique University/Industry consortium that is developing and providing licensing opportunities for novel sustainable technologies related to fuels and chemicals.

Subramaniam is associate editor of ACS Sustainable Chemistry and Engineering journal and chair-elect of the 2018 Gordon Research Conference on Green Chemistry. He has also served as the President of the International Symposia in Chemical Reaction Engineering (ISCRE, Inc.) and serves on the Board of Directors of the Organic Chemical Reactions Society (ORCS). His honors include ASEE’s Dow Outstanding Young Faculty Award, Indian Institute of Chemical Engineers’ Chemcon Lectureship Award, and KU’s Higuchi Research Achievement Award. Subramaniam is a Fellow of the AIChE, the ACS Industrial & Engineering Chemistry Division, and the National Academy of Inventors.

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