JOHNSON MATTHEY
TECHNOLOGY REVIEW

technology.matthey.com

Johnson Matthey Highlights

A selection of recent publications by Johnson Matthey R&D staff and collaborators

NON-PEER REVIEWED FEATURE

Received 19th September 2023; Online 9th October 2023

Flow Patterns of Ionic Liquid Based Aqueous Biphasic Systems in Small Channels

Y.-V. Phakoukaki, P. O'Shaughnessy, P. Angeli, *Chem. Eng. Sci.*, 2023, **265**, 118197

A kosmotropic salt and a hydrophilic ionic liquid were combined in water to form ionic liquid based aqueous biphasic systems (IL-ABS), and the flow of IL-ABS was studied in small channel systems for the first time. Different internal channel diameters and weight concentrations of the salt and ionic liquid were used to develop flow pattern maps. Dispersed, plug and parallel flow patterns were observed, which were shown to be influenced by both weight concentrations and channel diameter. Reynolds and capillary numbers were used to plot a generalised flow pattern map, where the transition boundaries of plug flow collapsed under all experimental environments.

Flow Regime Identification in Aerated Stirred Vessel Using Passive Acoustic Emission and Machine Learning

G. Forte, M. Antonelli, E. Brunazzi, M. J. Simmons, H. Stitt, F. Alberini, *Can. J. Chem. Eng.*, 2023, **101**, (10), 5670

Gas-liquid regimes were detected in a stirred, aerated vessel using a passive acoustic emission process sensor which incorporated novel machine learning (ML) approaches. Three identical cylindrical tanks, made from either aluminium, glass or steel, were used. A piezoelectric sensor was positioned on the exterior wall of each tank to measure pressure fluctuations (acoustic emissions). Rushton turbines were also installed. Impeller speeds and air feed flow rates were altered to investigate complete dispersion, loading, ungassed, flooding and flow regimes. The results were pre-processed using a PCA step and fed into three ML algorithms. By using the algorithms, the authors were able to successfully predict the three gas-liquid regimes of interest with an accuracy of 90–99%.

Cold Sintering of Bioglass and Bioglass/Polymer Composites

J. Andrews, G. Bullock, C. A. Miller, J. Booth, H. Ren, N. L. Kelly, J. V Hanna, I. M. Reaney, *J. Am. Ceram. Soc.*, 2023, **106**, (6), 3396

Current methods for generating bioglass-polymer composites, used to aid bonding of orthopaedic implants and regenerate bone tissue, have an upper limit of ~30 vol% bioglass. They also rely on controlled phase separation and dissolution of the polymer. To address this issue, the authors demonstrated a novel cold sintering (100ºC) process of Bioglass 45S5 powder. As-received, wetted and sintered samples of the glass powder were used in solid-state ^{31}P and ^{29}Si MAS NMR studies to investigate phosphorus and silicon speciation. Raman spectroscopy was also used, which provided an insight into the cold sintering densification mechanism.

Mapping Nanocrystalline Disorder Within an Amorphous Metal–Organic Framework

A. F. Sapnik, C. Sun, J. E. M. Laulainen, D. N. Johnstone, R. Brydson, T. Johnson, P. A. Midgley, T. D. Bennett, S. M. Collins, *Commun. Chem.*, 2023, **6**, 92

In this study, scanning electron diffraction was used to map the amorphous and crystalline components of Fe-BTC (BTC = 1,3,5-benzenetricarboxylate), a nanocomposite MOF renowned for its catalytic properties. The spatially separated atomic structure of the amorphous matrix was investigated with electron pair distribution function analysis. Systematic orientational disorder was observed within the nanocrystallites of Fe-BTC *via* Bragg

scattering analysis. Candidate unit cells were also identified for the crystalline component. Results from the separate structural analyses calculated disorder in Fe-BTC at the critical length scale for manufacturing composite MOF materials.

Process Parameter Optimisation for Manufacturing Porous Bioactive Silicate Glass Microspheres *via* Flame Spheroidisation: The Goldilocks Effect

M. T. Islam, A. J. Parsons, N. A. Nuzulia, Y. W. Sari, H. Ren, J. Booth, I. Ahmed, *J. Non-Cryst. Solids*, 2023, **614**, 122393

A series of characterisation techniques, including XRD, SEM and EDX, were used to examine the influence of flame spheroidisation process parameters on manufacturing porous and solid microspheres from bioactive 45S5 glass and 45S5 with the addition of viscosity modifiers. Comparisons were made with successfully processed phosphate glass microspheres. The results highlighted that process parameters such as cooling rate, starting particle size and gas flow rates had an important influence on the anticipated porous glass microsphere morphology. As a result, the authors proposed a processing model for the manufacture of highly porous microspheres from bioactive silicate glasses.

Net Zero Transition: Possible Implications for Catalysis

R. Bellabarba, P. Johnston, S. Moss, C. Sievers, B. Subramaniam, C. Tway, Z. Wang, H. Zhu, *ACS Catal.*, 2023, **13**, (12), 7917

The authors explore how the net zero energy transition will impact traditional chemical feedstocks and catalytic elements by mapping trends from pre-existing scenarios. For instance, the growth in electric vehicles will lead to changes in the supply and demand dynamics of critical materials such as rhodium, palladium and platinum. The demand for nickel and cobalt for energy storage applications could make them less attractive for catalytic applications. Decarbonisation of the chemical industry will be faciliated by the availability of carbon-free hydrogen and oxygen. The authors note that these disruptions must be reflected for the successful transition toward industrial sustainability.

Realizing the Continuous Chemoenzymatic Synthesis of Anilines Using an Immobilized Nitroreductase

S. C. Cosgrove, G. J. Miller, A. Bornadel, B. Dominguez, *ACS Sustain. Chem. Eng.*, 2023, **11**, (23), 8556

For the first time, a nitroreductase (NR-55) was shown to achieve aromatic nitro reduction in a continuous packed-bed reactor. Reuse of the immobilised system was accomplished through immobilisation on an amino-functionalised resin with a glucose dehydrogenase (GDH-101). A continuous extraction module was included which allowed the workup and reaction to be undertaken continuously in a single operation. An extension of this was demonstrated in a closed-loop aqueous phase which enabled the reuse of the contained cofactors. The application of this continuous biocatalytic method to panels of aryl nitro compounds could be a sustainable approach.

Carbon-Neutral and Carbon-Negative Chemical Looping Processes Using Glycerol and Methane as Feedstock

C. de Leeuwe, S. Z. Abbas, A. Amieiro, S. Poulston, V. Spallina, *Fuel*, 2023, **353**, 129001

The authors studied the potential for carbon-negative and carbon-neutral H_2 production through chemical looping reforming of glycerol and methane. The reforming experiments involved the reduction, oxidation and use of 500 g packed bed of oxygen carriers and the reforming process was tested at different temperatures and pressures. The maximum H_2 production was observed at 700ºC and 1 bar, with a H_2:CO ratio of 10. In a laboratory reactor setup, the authors successfully showed chemical looping steam reforming of methane with methane conversion >99%. Consecutive cycles rendered identical concentration and temperature profiles, thus verifying the feasibility and longevity of the process.

Catalytic Pyrolysis as a Platform Technology for Supporting the Circular Carbon Economy

C. J. Wrasman, A. N. Wilson, O. D. Mante, K. Iisa, A. Dutta, M. S. Talmadge, D. C. Dayton, S. Uppili, M. J. Watson, X. Xu, M. B. Griffin, C. Mukarakate, J. A. Schaidle, M. R. Nimlos, *Nat. Catal.*, 2023, **6**, 563

Catalytic pyrolysis, the process of combining vapour-phase catalytic upgrading and pyrolysis, has gained significant commercial and research attention in recent times. In the past decade, more than 15,000 patents and journal articles have been published on the topic. The attraction of catalytic pyrolysis is its ability to directly liquify waste plastic and biomass into intermediates, potentially leading to the decarbonised production of chemicals and fuels (**Figure 1**). The authors identify the long- and short-term technological barriers to implementing catalytic pyrolysis at a commercial scale. A development roadmap is proposed to address the barriers identified.

Interactions Between γ-Alumina Surfaces in Water and Aqueous Salt Solutions

O. Drecun, C. Bernardini, M. Sarwar, A. Striolo, *Colloids Surf. A*, 2023, **676**, 132152

The authors look into the interactions between

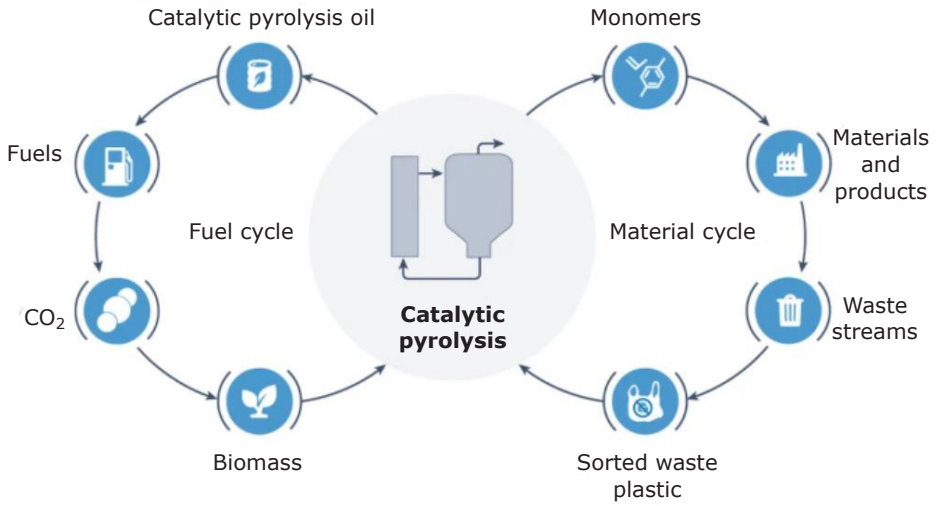

Fig. 1. Opportunities for catalytic pyrolysis as a circular carbon technology. Reprinted with permission from C. J. Wrasman *et al.*, *Nat. Catal.*, 2023, **6**, 563

agglomeration of gamma (γ) alumina nanoparticles in pure water alongside dilute aqueous salt solutions. The surface and salt- specific effects are characterised using the potential of mean force (PMF) profiles between γ-alumina surfaces ([110] and [100] facets) that are extracted using classical molecular dynamics (MD) simulations. Further experiments were carried out using dynamic light scattering (DLS) to study the macroscale agglomeration. The salts used are sodium chloride, ammonium acetate, barium nitrate and barium acetate. On particle surface contact, free-energy fluctuations of the PMF profiles show the structural changes of the aqueous phase. Values for the cohesive energy can be taken from the MD results which represent the interactions. The simulations formed correlate with the hydrodynamic radii of γ-alumina nanoparticles, these molecular scale findings were retrieved from the DLS experiments. The results show how the use of molecular simulations can be applied to identify the origins of macroscale observables.

Impact of Cylinder Deactivation Strategies on Three-way Catalyst Performance in High Efficiency Low Emissions Engines

G. Brinklow, J. M. Herreros, S. Z. Rezaei, O. Doustdar, A. Tsolakis, P. Millington, A. Kolpin, *Chem. Eng. J. Adv.*, 2023, **14**, 100481

The authors explore the use of cylinder deactivation (CDA) to reduce emissions as it is an important topic of discussion in the transportation sector currently. The authors also considered how the discussed strategies may influence catalyst performance. Two CDA strategies were employed. CO conversion improved to 100% and NH_3 formation over the catalyst was prevented in the first strategy of open-loop lambda control CDA. Using the closed-loop CDA strategy caused the catalyst temperature to increase by 300ºC for 60 s. The closed-loop CDA strategy has the possibility to increase catalyst temperature while reducing light-off during cold starts, without additional support, making it the better strategy to employ over other heating options. Both strategies provide opportunities to meet current and emerging regulations.

Order and Disorder in Cerium-Rich Ceria-Zirconia Solid Solutions Revealed from Reverse Monte Carlo Analysis of Neutron and X-Ray Total Scattering

A. Summer, H. Y. Playford, L. R. Owen, J. M. Fisher, A. Kolpin, D. Thompsett, R. I. Walton, *APL Mater.*, 2023, **11**, 031113

To analyse the distribution of cations and explore the possibility of oxide-ion disorder, two ceria-zirconia samples were analysed using reverse Monte Carlo analysis of neutron and X-ray total scattering data. The first material was heated in air (800ºC). The structure found was a single-phase solid-solution with the statistical distribution of cations. However, tetragonal symmetry was observed, consistent with the different coordination preferred by Ce and Zr. The second material was heated under hydrogen at 1050ºC and re-oxidised at 400ºC. The structure for this material showed great disorder with evidence for oxygen interstitials (Frenkel-ion defects) alongside a non-statistical distribution of cations with higher concentrations of like-to-like neighbours. This shows the existence of cation-rich nanodomains. The results showcase the dynamic nature of such solid-solutions that cause structural evolution once treated with heat. This is relevant to understand the practical applications of redox catalytic conditions and catalyst stability.