

Designing Porous Catalysts for Biomass Transformations

Karen Wilson,^{a*} Adam F. Lee^a

^a*School of Science, RMIT University, 124 La Trobe St, Melbourne VIC 3000, Australia*

**Corresponding author: k.wilson1971@googlemail.com*

Abstract: Catalyst design for the conversion of bioderived feedstocks to platform chemicals or fuels requires careful tailoring of materials to optimise pore structures to minimise mass transport limitations, improve hydrothermal stability under aqueous operation, and tune hydrophobicity to aid reactant or product adsorption/desorption. This presentation will describe how porous materials can be designed to tune these parameters, with a particular focus on the application of hierarchically porous solid acid catalysts in the pre-treatment and upgrading of bio-derived oils to transportation fuels.

Keywords: Solid acid, Biorefining, Solid base.

1. Introduction

Concerns over dwindling oil reserves, carbon dioxide emissions from fossil fuel sources and associated climate change is driving the need for clean, renewable energy supplies. If average global temperature rises induced by greenhouse gases are not to exceed 1.5 °C, then estimates indicate that a large proportion of crude oil, gas and coal reserves must remain untouched.¹ Biomass, derived from agricultural and forestry residues, or non-food sources of triglycerides are a sustainable source of carbon that can provide low cost solutions for transportation fuels and organic chemicals. Akin to petroleum refining, biorefining will integrate biomass conversion processes to produce fuels, power, and chemicals, thereby increasing the economic viability of bio-derived processes. Indeed, the US DoE identified a range of sugar derived ‘Platform Chemicals’ produced via chemical or biochemical transformation of lignocellulosic biomass that would be potential targets for production in biorefineries.² Catalytic technologies played a critical role in the economic development of both the petrochemical industry and modern society, underpinning 90 % of chemical manufacturing processes and contributing to over 20% of all industrial products. In a post-petroleum era, catalysis will underpin bio-refinery technology, and researchers will need to rise to the challenge of synthesising chemical intermediates and advanced functional materials and fuels from such non-petroleum based feedstocks.³

In contrast to fossil derived hydrocarbons, that require selective oxidation for chemical production, highly functional bio-molecules will require selective deoxygenation to form their target products. Commercial catalysts are not optimised for such reactions as they have been designed for conversion of petroleum derived molecules, and thus there is enormous scope for rationally designing improved heterogeneously catalysed processes tailored towards the production of bio-products and biofuels. To facilitate such a transition requires innovations in catalyst and process design for the selective conversion of these hydrophilic, bulky feedstocks into fuels and high-value chemicals. Catalyst development should focus on the use of tailored porous solids as high area supports to enhance reactant accessibility to active sites. To function effectively catalysts will also need to have tuneable hydrophobicity, be hydrothermally stable over a wide pH range, and resistant to in-situ leaching.

2. Experimental

Control of pore architecture was achieved through the use of mesoporous and meso-macroporous templated SBA-15 frameworks prepared by adopting methods of Zhao et al,⁴ and Vandreuil and co-workers respectively.⁵ Briefly, meso-macroporous SBA-15 (MM-SBA-15) was synthesised via a modified SBA-15 synthesis which included a hard macropore template of 100-500 nm polystyrene spheres. Details of the preparation of other catalyst systems discussed can be found in the relevant references below.

3. Results and discussion

This presentation will discuss the challenges faced in catalytic biomass processing, and highlight recent successes in catalyst design which have been facilitated by advances in nanotechnology and careful tuning of catalyst formulation. Specific case studies will explore how the effects of pore architecture and acid strength can impact upon process efficiency in biodiesel synthesis,⁶ and catalytic esterification pre-treatments of fast-pyrolysis oil in which short chain organic acids are removed to improve transportation fuel production. Macropore incorporation enhances esterification activity of SO₃H-SBA-15 for the upgrading of a real bio-oil derived from thermal fast pyrolysis of oak woodchips; the TOF for total organic acid removal increased three-fold relative to the mesoporous sulfonic acid silica, attributed to superior in-pore mass transport and active site accessibility (**Figure 1**).⁷

The role of bifunctional catalysts in the aqueous phase processing of sugars to important platform chemicals and fuel precursors such as 5-HMF derivatives will also be discussed.^{9,10} Bilayer SO₄-ZrO₂/SBA-15 catalysts will be reported, which are hydrothermally stable mesoporous materials offering high acid site loadings and enhanced 5-HMF productivity from glucose when compared to their non-porous SO₄-ZrO₂ (SZ) counterparts.¹¹ The co-existence of accessible solid basic/Lewis acid and Brønsted acid sites in grafted SZ/SBA-15 promote the respective isomerization of glucose to fructose and dehydration of reactively-formed fructose to 5-HMF.

4. Conclusions

The potential of lignocellulosic biomass for the production of renewable chemicals and advanced transportation fuels can only be unlocked via the development of tailored heterogeneous catalysts, in which advances in materials chemistry, nanoscience, surface chemistry and process engineering are exploited. Ultimately, catalytic chemists and engineers need to emulate the successes of heterogeneous catalysis in petroleum refining; achieving this necessitates an improved understanding of biomass properties and its impact on catalyst deactivation in order to accelerate biomass-to-chemicals and fuels production.

References

1. M. Jakob, J. Hilaire, *Nature*, 517, (2015), 150.
2. J.J. Bozell, G.R. Petersen, *Green Chem.*, 12, (2010), 539.
3. K. Wilson, A. F. Lee *Phil. Trans. R. Soc. A* 374, (2016), 20150081
4. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 279, (1998), 548.
5. S. Vaudreuil, M. Bousmina, S. Kaliaguine and L. Bonnevot, *Advanced Materials*, 13, (2001), 1310.
6. A.F. Lee, K Wilson, *Catalysis Today* 242, (2015), 3; J. Dhainaut, J-P. Dacquin, A.F. Lee, K. Wilson, *Green Chem.*, 12, (2010), 296
7. J.C. Manayil, A. Osatiashtiani, A. Mendoza, C.M.A. Parlett, M.A. Isaacs, L.J. Durdell, C. Michailof, E. Heracleous, A. Lappas, A.F. Lee, K. Wilson, *Chem.Sus.Chem.*, 10, (2017), 3506.
8. L. Ciddor, J.A. Bennett, J.A. Hunns, K. Wilson, A.F. Lee, *J. Chem. Tech. and Biotech.*, 90, (2015), 780
9. A. Osatiashtiani, A.F. Lee, D.R. Brown, J.A. Melero, G. Morales, K. Wilson, *Cat. Sci. & Tech.*, 4, (2014), 333.
10. G. Morales, A. Osatiashtiani, B. Hernandez, J. Iglesias, J.A. Melero, M. Paniagua, D.R. Brown, M. Granollers, A.F. Lee, K. Wilson, *Chem. Commun.*, 50, (2014), 11742
11. A. Osatiashtiani, A.F. Lee, M. Granollers, M., D.R. Brown, L. Olivi, G. Morales, J.A. Melero, K. Wilson, *ACS Catalysis*, 5, (2015), 4345.

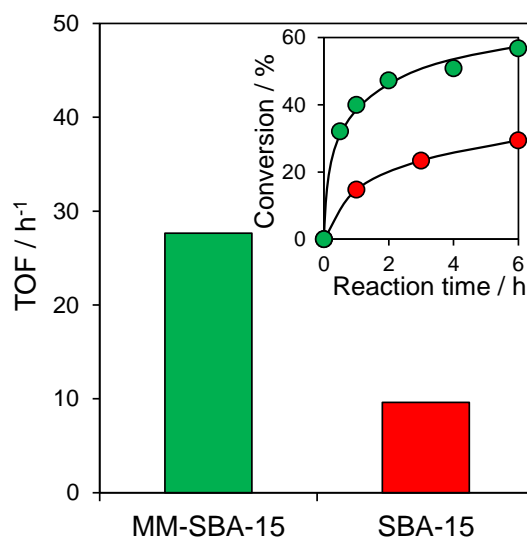


Figure 1. Effect of support architecture on the TOFs of sulfonic acid catalysed bio-oil esterification. Inset: acid conversion profiles for bio-oil esterification using sulfonic acid catalysts. (Reaction conditions: 9.2 g bio-oil \approx 10 mmol acid, 12.1 ml MeOH (Acid:MeOH molar ratio = 1:30), 100 mg catalyst, 85 °C)