Starbons® - A New Family of Bio-based Mesoporous Materials Derived from Polysaccharides

J.H. Clark, V.L. Budarin, S.W. Breeden and D.J. Macquarrie

Green Chemistry Centre of Excellence, University of York, York YO10 5DD, UK and Starbons Ltd, York Science Park, York YO10 5DD, UK

ABSTRACT

Porous carbon materials have been prepared which a wide range of technologically important applications, including separation science, heterogeneous catalyst supports, water purification filters, stationary phase materials, as well as energy generation and storage applications. Templated routes to ordered mesoporous carbons are well established, but the surface of the material is difficult to chemically post-modify and processing is energy and resource intensive and laborious. The production of carbon materials from biomass (i.e. sugars or polysaccharides) is a relatively new but rapidly expanding research area. Here we describe mesoporous polysaccharide-derived ‘‘Starbons’’ carbonaceous material technology which is based on food waste valorization and yielding materials with flexible surface chemistries and remarkably mesoporous structures.

Keywords: Starbons®, mesoporous, polysaccharides, catalysis.

1 BACKGROUND AND KEY PROPERTIES

A novel approach for the generation of a new family of mesoporous carbonaceous materials is that based on expanded polysaccharides (hereinafter referred to as “Starbon®”) [1]. This novel Starbon® technology utilises the natural ability of polysaccharides to retain their organized structure on pyrolysis (Starbon® has been registered by the University of York as a trademark in the UK). The process for manufacture consists of three simple steps: i) gelatinisation; ii) retrogradation; iii) acid-catalysed carbonisation. By adjusting the temperature at which the carbonisation is carried out, a continuum of materials is produced. This process is gentle and provides the opportunity to produce a range of mesoporous carbon-based materials from starch like materials to porous graphitic carbons, including amorphous oxygen-containing carbons as can be seen in Figure 1.

Starbon® Technology is:

- Sustainable: polysaccharides are renewable and widely available in many countries often in (eg food) waste streams
- Simple: three stage methodology: gelatinisation, dehydration and controlled pyrolysis
- Non-persistent, non-bioaccumulative and non-toxic

Properties of Starbons® include:

- Tuneable surface functionality
- High surface areas & mesoporosity (up to 500 m^2 g-1, 8-15 nm pore diameter, pore volume up to 2.0 cm3 g^{-1}
- Controllable electrical conductivity
- Particulate / monolithic forms

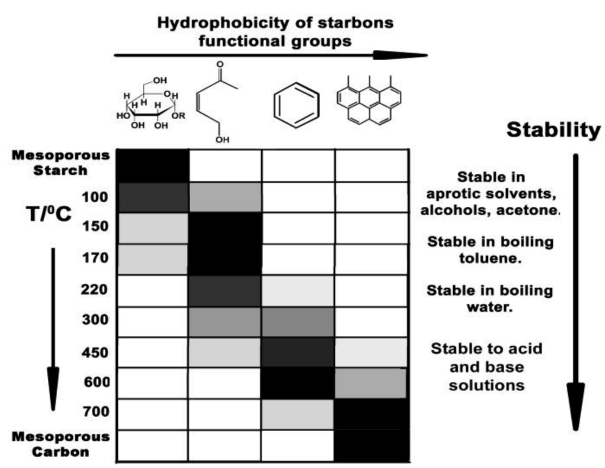

Figure 1: Diagram showing surface functionality with temperature preparation, and materials applications.

2 STARBON® APPLICATIONS

Information about mechanism of starch decomposition gives us opportunity to predict the temperature of Starbons® preparation for certain applications. The remaining starch functionality within Starbons® up to 250˚C enables the possible use of these materials in applications typical to starch such as chromatographic separation of enantiomers. Preliminary studies have confirmed that they are effective as a stationary phase for liquid chromatography, allowing separation of a standard test mixture of substituted ferrocene compounds.

Low temperature prepared sulfonated aromatic carbonaceous materials have recently been shown to be effective solid acid catalysts and, as Starbons® prepared between the temperatures of 300 and 600º have aromatic functionality, sulfonation of these materials should also result in useful solid acid materials. Remarkably, we have found that the reactions of carboxylic diacids in aqueous alcohol demonstrate the excellent activities and particular characteristics of Starbon® acids. Esterification reactions of organic diacids in water were chosen because they can offer several interesting features. Firstly, (di)carboxylic acids are included in the top biomass platform molecules as forecast for near future large scale applicability. Secondly, esterifications are one of the most useful transformations for organic acids, especially for a dicarboxylic acid since the diester can be used as an intermediate in the manufacture of polymers. Thirdly, traditional esterification methods are unselective, use soluble mineral acids that have to be separated at the end of the reaction, and lead to hazardous waste.[1]

Starbon® acids based on Starbons® prepared at different temperatures showed an optimum catalytic activity for each one of the diacids screened in the esterification, with sharply reduced activities below or above this maximum. Perhaps the most interesting feature of the Starbon® acids catalysis is the substrate-dependent maximum of catalytic activity. Activities peaked at ca 400°C (succinic), 450ºC (fumaric) and 550ºC (itaconic acid).

A further application for Starbons® is as a solid carrier for precious metal catalysts [2]. We have found that palladium metal supported on starbons is as an active catalyst for a model Heck reaction of iodobenzene with methyl acrylate. Again, the importance of the control over the surface chemistry of these materials is apparent: Starbon® prepared at 220˚C proved the most effective for this reaction.

The pore structure of Starbons® also makes them excellent separation media. In particular those derived from alginic acid have internal structures that make them potential alternatives to commercial porous graphitic carbons which are expensive and involve high-energy demanding manufacturing processes [3].

Alginic acid-derived Starbon® pyrolysed to 800 ºC were analysed by *in-situ* TEM which showed the development of turbostratic graphite from 550 ºC, a catalysed process attributed to calcium nanoparticles present in the structure Commercial PGC separation of five carbohydrates (mannitol, sucrose, maltitol, raffinose and stachyose) was compared against a Starbon® column and the Starbons® materials proved to be comparable with the elution order, although the Starbon® column also appears to partially separate the carbohydrates raffinose and stachyose, better than the commercial material.

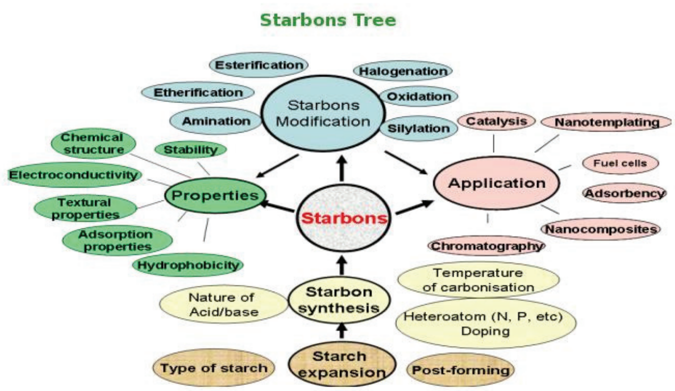

Figure 2: Starbon Tree of properties and applications

3 CONCLUSIONS

Starbons® are a unique family of materials with tuneable properties that make them suitable for a wide range of applications (Figure 2). Starbons® is now a spin-out company from the University of York

REFERENCES

[1] Budarin, V., Clark, J. H., Hardy, J.J., et al, Angew Chemie Intn Edn., 2006, **45**, 3782-2786.

[2] White, R.J., Luque, R., Budarin, V., Clark, J.H., et al, Chem.Soc.Rev., 2009, **38,** 481-494

[3] White, R.J., Antonio, C., Budarin, V.L., Bergstrom, E., Thomas-Oates, J., & Clark, J.H. , 2010, **20**, 1834-1