Institution: The University of Huddersfield

Unit of Assessment: 8 Chemistry

Title of case study: New Thermal Methods for Materials Preparation and Characterisation

1. Summary of the impact

Methods to improve control over thermally-induced solid state transformations have been developed in Huddersfield and applied to materials synthesis and materials characterisation. Impact is being felt by catalyst and adsorbent manufacturers, where feedback-controlled thermal and microwave methods allow improved control of morphology, surface area and porosity, and possibly the nature of surface sites. New thermal characterisation methods, some based on these principles, plus calorimetric adsorption, modulated differential calorimetric and high speed thermal methods, are being applied to catalytic/adsorbent materials. The information arising from these studies is bringing economic benefit to manufacturers. The same techniques are also being applied to pyrotechnic materials, in work which has been credited with making a significant contribution to defence research in the UK and overseas.

2. Underpinning research

P A Barnes (Emeritus Professor, retired 2007, Professor 1997-2007), E L Charsley (Emeritus Professor, retired 2010, Professor 1997-2010), D R Brown (Professor 2003- and Reader 1997-2003) and G M Parkes (Reader 2011-, Senior Lecturer 2002-2011, Research Fellow 1997-2002) have been developing new thermal techniques for both solid materials preparation (thermal processing), and materials characterisation (thermal analysis) since 1997. The reason this work is important is that, when using standard or conventional thermal methods, variations in temperature across the bulk of solid materials limit 1) the control that is available in materials synthesis and 2) the information that is available from characterisation techniques. **The new thermal techniques (including various “controlled-rate” processes, using both conventional and microwave heating) have allowed increased control in synthesis, and increased precision in characterisation, leading to finer control of material properties and better understanding of many thermally-induced solid-state processes.**

Barnes and Parkes (1997-2009) developed controlled-rate methods of thermal analysis in which the heating regime is continuously controlled by feedback from the rate of the thermally-induced reaction of a solid sample, [A1, A2] greatly improving the quality of information provided. The techniques were extended to control not just heating programmes but also, for example, over-gas compositions. [Grants G1, G2]

The techniques were scaled-up for materials preparation, firstly in carbon and impregnated carbon activation (Dstl 1997-, BAT 2003-), and latterly through controlling calcination techniques for catalyst synthesis more generally. [A3] [Grants G3-G6] Barnes, Parkes and Charsley, over 1997-2004, applied controlled-rate algorithms to microwave thermal analytical techniques [Grants G7-G10], where they offer the particular benefit of precise temperature control even when sample dielectric properties are changing. Adapting microwave controlled-rate methods to semi-preparative and then preparative scale took place over 2004-2009. Current work (Brown and Parkes) is focussed on microwave-induced controlled production of mixed metal oxide catalysts through calcination of the hydroxides. [A4] These dehydration processes involve large changes in microwave coupling and, without controlled-rate technology, temperature control is not possible.

More widely, solid materials characterisation has been facilitated by the development and refinement of adsorption calorimetric techniques by Brown (1997-). [A5] [Grants G11-G13] These techniques provide unique information on the abundance, strength and strength distribution of active sites on the surfaces of solid catalysts and adsorbents. Two approaches have been used, based on 1) the progressive adsorption of probe gases from a flowing carrier gas and 2) the progressive adsorption under static conditions where adsorption equilibrium is achieved at each stage of the addition of probe gas. The unique capability in this area held at Huddersfield has led to almost 40 papers, and many academic and industrial collaborations.

In another area in which our novel thermal methods have been applied to chemical systems in new ways, Charsley has studied metal-oxidant pyrotechnic reactions (1997-date). He has used both the new thermal methods described above and other specialised thermal techniques designed for studying these very reactive materials, such as modulated temperature differential calorimetry and sample ignition-controlled thermal analysis. [Grants G14-G16] The use of these techniques, in conjunction with chemical analysis, has proved to be an effective approach to investigating the reaction mechanisms of a wide range of pyrotechnic systems and has been extended to studying the mechanism of ageing under ambient conditions in collaboration with industrial partners (e.g. QinetiQ, 1998-2009). [A6]

3. References to the research (*key papers bold/starred*)

[A1]* M Tiernan, P A Barnes, and G Parkes, *Reduction of iron oxide catalysts: the investigation of kinetic parameters using rate perturbation and linear heating thermoanalytical techniques*, (2001), *J. Phys. Chem. B*, **105**, 220. 10.1021/jp003189+

[A2]* E A Fesenko, P A Barnes, G M B Parkes, D R Brown and M Naderi, *A New Approach to the Study of the Reactivity of Solid-Acid Catalysts: The Application of Constant Rate Thermal Analysis to the Desorption and Surface Reaction of Isopropylamine from NaY and HY Zeolites,* (2001), *J. Phys. Chem. B*, **105**, 6178. 10.1021/jp004587f

[A3] E A Dawson, G Parkes, P A Barnes, M Chinn, A Pears and C Hindmarsh, *A study of evolved gas control and its effect on carbon yield during the activation of carbon fibres by controlled rate methods*, (2002), *Carbon*, **40**, 2897. 10.1016/S0008-6223(02)00220-8

[A4] H E Cross, G M Parkes and D R Brown, *Microwave calcination of Cu/Mg/Al hydrotalcite catalyst precursor*, (2012), *Appl. Catal.*, **439-430,** 24. 10.1016/j.apcata.2012.03.046

[A5]* M P Hart and D R Brown, *Surface Acidities and Catalytic Activities of Acid-Activated Clays,* (2004), *J. Mol. Catal. A: Chem*., **212**, 315. 10.1016/j.molcata.2003.11.013

[A6] I M Tuukkanen, E L Charsley, S J Goodall, P G Laye, J J Rooney, T T Griffiths, H Lemmetyinen, *An investigation of strontium nitrite and its role in the ageing of the magnesium–strontium nitrate pyrotechnic system using isothermal microcalorimetry and thermal analysis techniques*, (2006), *Thermochim. Acta*, **443,** 116. 10.1016/j.tca.2006.02.004

External funding supporting underpinning research:

[G1] EPSRC: 1997-2001 (£182,000) *Enhanced thermal methods and their application in catalysis* (PI: P A Barnes). GR/66069/01.

[G2] ICI (now JM): 1998-2001 (£156,000) *Controlled rate thermal methods in catalyst preparation* (PI: P A Barnes).

[G3] DERA, MOD: 1997-2000 (£440,000) *Novel modified carbon adsorbents* (P A Barnes)

[G4] Dstl: 2003-05 (£80,000) *Activated carbon porosity using controlled rate thermal methods* (PI: P A Barnes).

[G5] Dstl: 2012- (£25,000) *The use of gas adsorption calorimetry to characterise the interaction of selected TICs on carbon and other adsorbents* (PI: G M B Parkes and D R Brown).

[G6] BAT Ltd 2008-10 and 2010-2012 (£199,000) *Creation of mesopores in activated coconut carbon* (PI: G M B Parkes).

[G7] Royal Society of Chemistry: 1999-2002 (£33,000) *Microwave thermal analysis* (PI: P A Barnes).

[G8] EPSRC: 1997-1999 (£85,000) *New methods of thermal analysis using microwave heating/detection* (PI: P A Barnes). GR/K99862/02.

[G9] EPSRC: 2002-05 (£249,000) *An instrument for the quasi-simultaneous measurement of the temperature dependence of dielectric parameters* (PI: P A Barnes). GR/R38460/01.

[G10] Home Office CBRN S&T: 2005-8 (£340,000) *Removal of toxic gases from air streams using pulsed microwave activation of novel catalytic materials* (PIs: G M B Parkes, P A Barnes) Project ref: TR23/04/02.

[G11] DTI/EPSRC LINK: Catalysis and catalytic processes 1998-00 (£494,000) *Sulfonated organic resin acid catalysts* (PI: D R Brown with Purolite Intl). GR/L87859/01.

[G12] MEL Chemicals: 2008 (£18,000) *Modified zirconia auto catalysts* (PI: D R Brown).

[G13] MEL Chemicals: 2011 (£25,000) *New applications of* Li_2ZrO_3 (PI: D R Brown).

[G14] DERA / QinetiQ Ltd: UK 1998-2009 (£800,000) *Thermal characterisation of pyrotechnic systems* (PI: E.L.Charsley).

[G15] armasuisse, Switzerland: 2001-2010 (£133,000) *Thermal studies on pyrotechnic systems* (PI: E.L.Charsley).

[G16] Finnish Defence Forces 2001-2005 (£102,500) *Ageing behaviour of magnesium pyrotechnic compositions* (PI: E.L.Charsley).

4. Details of the impact

Impact has been generated by two routes. The first is through the synthesis of porous solids and the capability for tuning porosities in both adsorbent and catalyst synthesis. The second is through improvements to thermal analytical techniques and the new information available on the structure/function relationships in solid-state systems. The techniques have been used in the characterisation of catalytic materials and pyrotechnic materials, with the associated benefits to users and to manufacturers, including global companies and the defence industry.

We have been working with Johnson Matthey (JM) since 1999 (as ICI/Synetix in the early years), applying controlled-rate techniques to catalysts and catalyst precursors with a view both to strengthening the understanding of the processes that occur in the preparation of solid catalysts and to improving the properties of solid catalysts prepared by thermal methods. Our (Parkes' and Barnes') work with JM, based on that reported in references A1-A3 above, has illustrated the potential for controlling catalyst morphology, especially in calcined materials, so offering the prospect to tune key catalyst properties. Through both our early fundamental work and the continuing collaboration with JM, knowledge transfer to JM has occurred. Impact has been felt by JM throughout the assessment period and continues to be felt today. The Catalysis R and D Director at JM, describes the research as "***crucial for our understanding of how to scale and optimise manufacturing processes for materials development. This has clear implications for economic and environmental benefits for our manufacturing processes and end-users of our products***".[S1]

Joint research with Dstl, Porton Down over a similar period (Parkes and Brown) has been aimed at the use of controlled-rate techniques to tailor porosity characteristics in activated carbons. The objectives were to increase understanding of the synthesis/preparative factors that control the properties of carbon adsorbents, and also to improve the extent to which activated carbons can be characterised. This work (reference A3 above) was ultimately aimed at improving carbon adsorbents for personal respirator use by improving the balance between effective adsorption performance and resistance to airflow. The benefits in these directions were witnessed at Dstl in the 2008-2010 period and the Chief Scientist (Physical Sciences Dept), Porton Down, reports that: .... *(Our collaborative work) "has greatly increased our understanding of the factors that affect the performance of activated carbons used in respirator filters including the influence of metal impregnants and pore structure on removal of toxic chemicals from contaminated airstreams. In particular the* ***controlled-rate activation methods developed at Huddersfield have enabled excellent control over the properties of activated carbons, resulting in significant improvements in adsorbent performance and their long-term stability"***.[S2]

A similar approach to tuning carbon pore structures using controlled-rate techniques has recently been applied to carbon adsorbents for use in cigarette filters (2008-date, funded by BAT). [B1] The joint research (Parkes) has shown that it is possible to change the internal structure of an activated carbon derived from an environmentally-preferred vegetable-based source to maximise its adsorption properties when operating under high flow rates. The Research Manager at BAT confirms that in the period since 2010 *"significant enhancements in the adsorption of some key smoke toxicants were achieved* (using the methods developed in Huddersfield) *compared to the use of conventional materials".*[S3] An international patent with BAT has been granted. [B2]

Our expertise and unique capability in adsorption calorimetric techniques have been applied to work with MEL Chemicals (Brown). Over the period from 2003 we have been using these techniques, based on references A4 and A5 above, to characterise modified zirconia catalysts, significantly increasing the company's understanding of the structure/function relationship in these materials. Impact has been felt in two areas. The first is in designing doped zirconias with controlled acidity/basicity for use mainly in auto catalysts but also in gas clean-up catalysts [B3] (2008-2011). The second is in the design of lithium zirconate catalysts for biodiesel synthesis (2011-13). A patent was filed on our joint work on lithium ziroconate in 2012 [B4] and the work has been presented at numerous conferences. The Divisional Research and Development Director says that this work has ***"strengthened our product range. In monetary terms, the joint research has certainly brought benefit to MEL***".[S4]

Over the period 2000 to date, Charsley has been carrying out research with the Defence Evaluation and Research Agency, QinetiQ Ltd, armasuisse, Switzerland and the Finnish Defence Forces. In this work a series of advanced and unique thermal analytical techniques (based on reference A6 above) have been used to characterise the strongly exothermic reactions of a range of pyrotechnic compositions, with a view to designing new materials using more benign compounds than those that have traditionally been used, particularly perchlorates. [B5] This has resulted in a series of new formulations (introduced 2008-2010) based on magnesium alloy-sodium nitrate-calcium resinate compositions. The overall programme was sponsored by the Strategic Environmental Research and Development Programme (SERDP), US Department of Defence and in 2009 was awarded the **SERDP Project of the Year Prize**. The Principal Capability Group Leader at QinetiQ involved in this work confirms that the contribution of Huddersfield "*was pivotal to the consortium being awarded the project (in competition with US research laboratories) and the prize",* adding that *"the reputation of your team and quality of work performed at Huddersfield has allowed the UK to benefit from a number of long term international collaborative studies on pyrotechnics and novel materials".* [S5] Through facilitating the study of these reactive materials, says QinetiQ, the University has "***contributed to defence research both in the UK and internationally".***

5. Sources to corroborate the impact

References (from section 4)

[B1] E A Dawson, G M B Parkes and P Branton, *Synthesis of vegetable-based activated carbons with mixed micro-and mesoporosity for use in cigarette filters,* (2012), *Ads.Sci.Technol*., **30**, 859. Joint Huddersfield/BAT(Branton). http://eprints.hud.ac.uk/16683/

[B2] P Branton, E Dawson and G Parkes, *Method of preparing porous carbon*, PCT/GB2011/050882. Patent authors from Huddersfield and BAT (Branton).

[B3] H Stephenson, E Dvininov, D R Brown, *Alkaline zirconate for biodiesel production*, Patent Application No 12091145.0, filed 24 May 2012. Patent authors from Huddersfield and MEL (Stephenson, Dvininov). Search report received. Decision pending on re-filing.

[B4] Several papers/reports were published jointly by MEL and VTT, Finland on the gasification of biomass. Our work on zirconia catalyst characterisation was used in these projects. E.g. T Viinikainen, H Ronkkonen, H Bradshaw, H Stephenson, S Airaksinen, M Reinikainen, P Simell and O Krause, *Acidic and basic surface sites of zirconia-based biomass gasification gas clean-up catalysts*. (2009), *Appl. Catal. A*, **362**, 169. 10.1016/j.apcata.2009.04.037

[B5] Charsley (Huddersfield) and Griffiths (QinetiQ) presented joint work at numerous conferences and events. E.g. T T Griffiths, E L Charsley, H M Markham and J J Rooney, 36th International Pyrotechnics Seminar, Rotterdam, TNO Defence, Security and Safety, 2009, 377. *Pyrotechnic incendiary compositions*.

Sources of supporting letters (referred to in section 4). Names provided separately.

[S1] Technology Manager and Catalysis R and D Director, Johnson Matthey PCT. Oversaw all the collaborative projects with ICI Katalco, Synetix and now Johnson Matthey, on application of controlled-rate methods to catalyst synthesis, including carbon-supported materials, and can speak on the outcomes and impact of the work.

[S2] Chief Scientist, Dstl, Porton Down. Responsible for research on adsorbents for gas filtration and can verify impact of controlled-rate thermal methods on activated carbon adsorbent preparative methods, and can confirm importance of adsorption calorimetric methods in characterising adsorbent materials.

[S3] Research Manager, Group Research and Development, British American Tobacco. Can verify impact of controlled-rate thermal methods on the tuning of carbon adsorbent properties for toxin adsorption from tobacco smoke.

[S4] Divisional Research and Development Director, MEL Chemicals. Can describe the influence our research, especially adsorption calorimetric methods, has had on design of doped zirconias for both auto and other catalytic applications, and can also verify impact of joint development of lithium zirconate biodiesel catalysts.

[S5] Principal Capability Group Leader, QinetiQ, Fort Halstead. Can verify the impact of our work on pyrotechnic storage and on environmentally improved pyrotechnic compositions, and can also confirm the importance of SERDP prize to QinetiQ and UK defence research.