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# Surface polymerization of perfluorosilane treatments on paper mitigates HF production upon incineration†

Stephanie Oyola-Reynoso,<sup>a</sup> Jiahao Chen,<sup>ab</sup> Boyce S. Chang,<sup>a</sup> Jean-Francis Bloch<sup>d</sup> and Martin M. Thuo<sup>\*abc</sup>

Hydrophobic paper has inspired advances in low-cost technologies. Of importance is the use of perfluorinated reagents, due to suspected release of HF. Surprisingly, by using a coupled TGA-IR-MS, we demonstrate that polymerization of a perfluorinated silane on paper, leads to rapid degradation, low-ash residue, and no toxic HF gas is produced under thermolysis.

Increased interest in paper based devices, especially in low-cost diagnostics, calls for a better understanding of the effect of the various forms of treatment deployed on the overall behaviour of the material. Safety, and eventual degradation, are vital especially in biomedical waste management. Recently, organo-fluorine<sup>1</sup> compounds have been adopted for surface modification of paper due, in part, to their hydrophobicity and ease of use.<sup>2–5</sup> Fluorine based reagents, however, can form toxic hydrogen fluoride (HF) or hydrofluoric acid when mixed with water or upon degradation.<sup>6</sup> HF penetrates the skin and insidiously destroys underlying body tissues. Fluoride ions will also react with minerals such as calcium and magnesium in the body to form insoluble salts.<sup>7</sup> Furthermore, HF fumes will damage lung tissue if inhaled.<sup>7</sup> Despite these hazards, fluorine based reagents have been used for different applications such as coatings and modifying wetting properties of porous materials, like paper.<sup>8–14</sup>

Recently, paper has gained interest as a substrate for biomedical devices fabrication,<sup>14</sup> partly because it is ubiquitous and is affordable.<sup>15</sup> Paper chemistry is also well understood and,

as such, can be readily functionalized, especially through surface hydroxyls. We<sup>16–19</sup> and others are interested in fabricating hydrophobic paper-based devices using perfluoro alkylsilanes (Fig. 1a).

We recently showed that when trichloro perfluoro octylsilane reacts with paper, surface bound water is recruited as a comonomer leading to self-assembly driven chemi-sorption of polymeric gel particles ranging from nanoscale to full surface coverage (Fig. 1b).<sup>19</sup> Size of resulting polymer particles coupled with inherent anisotropy of the paper fibers leads to surfaces with tuneable chemi-sorption of polymeric gel particles (from nanoscale to full surface coverage).<sup>19</sup> Size of resulting particles coupled anisotropy of the paper fibers leads to surfaces with tuneable wettability. Despite wide use of perfluorinated organosilanes in surface modification of cellulosic materials, little has been investigated in terms of their thermal degradation, in part due to an assumption that toxic HF would be generated. In fact, Glavan *et al.*<sup>20</sup> speculated (from elemental analysis of the functionalized paper) that thermal degradation of 1 cm<sup>2</sup> of the perfluoro silane treated paper could yield as much as 29 µg HF (at  $T < 1500$  °C) or a maximum of *ca.* 49 µg COF<sub>2</sub> when degraded at high temperatures.<sup>20</sup> This was a speculation based on the

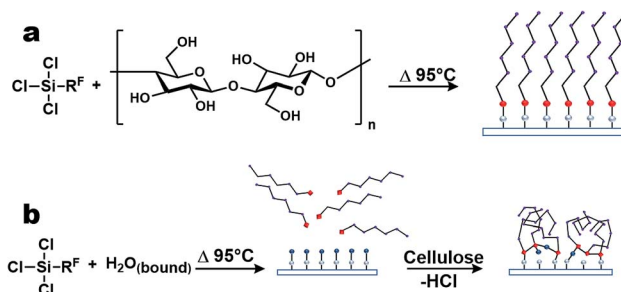


Fig. 1 (a) Previous reports suggest that silane attaches to cellulose forming a monolayer. (b) Recently determined reaction between silane and bound water on cellulose. The mechanism shows that an oligomer/polymeric gel particles are formed due to crosslinking and self-assembly of the fluoro alkyl silanes.

<sup>a</sup>Department of Material Science and Engineering, Iowa State University, Ames, IA 50011, USA. E-mail: mthuo@iastate.edu

<sup>b</sup>Micro-Electronic Research Center, Iowa State University, 133 Applied Sciences Complex I, 1925 Scholl Road, Ames, IA 50011, USA

<sup>c</sup>Biopolymer and Biocomposites Research Team, Center for Bioplastics and Biocomposites, Iowa State University, 1041 Food Sciences Building, Ames, IA 50011, USA

<sup>d</sup>Grenoble Institute of Technology, 461 Rue de la Papeterie, 38402 Saint-Martin-d'Heres, France

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assumption that thermal degradation of the material proceeds as though the organofluoro compound were in its free state. Also, there was no indirect evidence (or cited literature) to support whether the fluorinated material will degrade to give off HF even under incineration.

We hypothesized and demonstrated that when paper is modified by silanes, the results is a cross-linked polymeric material, that can organize into small particles and eventually, upon confluence, forms a film.<sup>19</sup> Thermal degradation of the perfluorosilane treated paper, should therefore be considered in light of a polymeric film. To this end, we hypothesized that the polymerized material can either undergo breakdown to form hydrophobic silicon oxide films as recently observed with silicone polymers,<sup>21</sup> or a depolymerisation would ensue to relieve steric strain.<sup>22,23</sup> Depending on the temperature at which depolymerisation occurs, the organofluoro compounds may be distilled off before they thermally degrade averting the production of HF or other fluorocarbon derivatives.

## Materials and methods

### Materials

1H,1H,2H,2H trichloro(perfluorooctyl)silane was obtained from Sigma-Aldrich and was used as received.

### Surface modification

Surface control polymerization was performed on a high grammage blotting paper (NYX Los Angeles CA) that was cut into small pieces ( $\sim 1 \times 1$  cm in diameter). The high density paper was then placed on a warm desiccator containing Drierite. A vial containing 1H,1H,2H,2H trichloro(perfluorooctyl)silane (100  $\mu$ l) was placed inside the desiccator. The desiccator was sealed and evacuated allowing the reaction to occur *in vacuo*. The system was then immediately placed in an oven maintained at 368 K. The reaction was then allowed to equilibrate and proceed at these conditions for a prescribed period of time. On expiration of the reaction time, vacuum was released and sample removed from the chamber and the success of the treatment was assessed by placing the treated papers under water.

### Gas phase analysis

Coupled TGA/DSC-FTIR-MS (Netzsch STA449F1) was used to investigate products of thermal decomposition of treated paper samples. Thermal analysis was performed with a tungsten furnace (RT – 2400 °C) at a resolution of 0.025  $\mu$ g and heating/cooling rates of (40 °C to 800 °C) 20.0 K min<sup>-1</sup>. Samples were placed in alumina crucible, heated and the exudates analyzed in real time. Collected data was analyzed using the Proteus® Software. Purge gas was composed of constituted air (nitrogen-oxygen-nitrogen) (Airgas, Inc.). An intake flow of 10–10–40 ml min<sup>-1</sup> respectively. FTIR of the evolved gases from the decomposition of treated cellulose was performed on a Bruker system (Tensor 37 model). OPUS software was used to analyze the data. MS from the evolved gases was collected and analyzed with Aeolos software.

### Liquid phase analysis

Surface treated paper was placed into a long-neck volumetric flask and the setup was heated above 700 °C. The distillate was then washed down with deuterated chloroform. The solution was analyzed by <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F nuclear magnetic resonance (NMR).

## Results and discussion

To test our hypothesis, we prepared and characterized modified paper using a trichloro perfluorooctyl silane. This paper experimentally demonstrates that when the silane is polymerized and the paper is incinerated at  $T \leq 800$  °C there is no significant amount of HF produced. We treated high grammage paper (163.76 g m<sup>-2</sup>) with (1H,1H,2H,2H trichloro(perfluorooctyl)silane) (abbreviated TFOS, 97%, Sigma-Aldrich) at different reaction times and *in situ* characterized the products upon thermal degradation using a coupled TGA-IR-MS. Based on the above discussion, and the deployed analysis, peaks at  $M + 1 = 20$  (HF) and  $M + 1 = 66$  (COF<sub>2</sub>) were expected from the mass spectrum of the thermally degraded fluorinated paper samples. These  $m/z$  peaks would be confirmed by observation of IR signals at 1700 cm<sup>-1</sup> (C=O) accompanied by a broad peak at 3600–4000 cm<sup>-1</sup> (HF). To evaluate this hypothesis, high grammage paper was treated with TFOS vapours for 24 h at 95 °C.

Thermogravimetric analysis (TGA) was performed at a heat rate of 20 °C min<sup>-1</sup> from 40 °C up to 800 °C in air. To diminish potential interference by adventitious moisture, IR and MS analysis were started at 100 °C. The TGA results revealed two stages of thermal decomposition at 330 °C and 430 °C for both the untreated (control) and treated samples (Fig. 2a). Interestingly, we observe that the treated samples showed higher mass loss than the untreated (90% vs. 65%) over the same temperature range. This difference is observed irrespective of the time the paper is treated with the silane – which has been shown to correlate with the amount of chemisorbed silane. These results are counterintuitive as they suggest that surface modification may enhance thermal degradation of the paper – reduced residual ash. The difference in percentage weight loss is not specific to either the 330 °C or the 430 °C regions although, in the treated papers, a noticeable difference in the onset of the second degradation region is observed. This discrepancy in the total mass loss may be, in part, due to reduction of filler materials in paper upon reaction with the silane reagent. The presence of these fillers (mostly calcium carbonate) can interfere with the thermolysis, producing more char compared on the untreated paper.

This discrepancy in the total mass loss may also, in part, be due to differences in physi-sorbed adventitious contaminants on the two types of surfaces, with the untreated paper (higher surface energy  $\gamma > 70$  mN m<sup>-1</sup>) potentially attracting a larger variety of contaminants than the treated ( $\gamma \sim 25$  mN m<sup>-1</sup>).<sup>24</sup> Alternatively, it could imply that presence of the hydrophobic coating enhances thermal decomposition – to our knowledge, there is no known combustion mechanism that explains how this would occur. Although the TGA shows two regions of

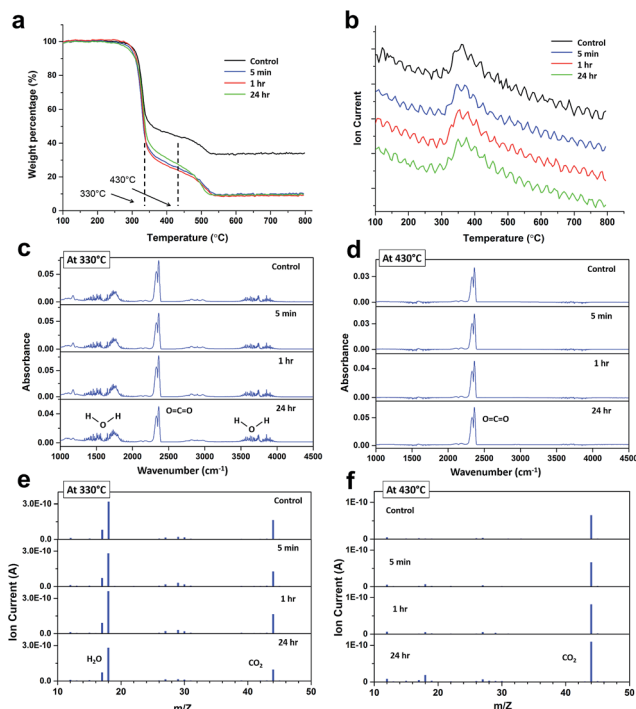


Fig. 2 Paper based samples treated with a fluorinated alkyl silane reagent for different periods of time analysed upon incineration in air. (a) Thermogravimetric analysis (TGA) from 100 °C to 800 °C. (b) Total ion current from 100 °C to 800 °C. (c–d) FTIR spectrum from 1000  $\text{cm}^{-1}$  to 4500  $\text{cm}^{-1}$  at 330 °C and 430 °C. (e–f) Mass spectrum at 330 °C and 430 °C.

thermal degradation, occurring at different rates of mass loss, the Graham–Schmidt plot shows an overlap in the total number of exudates (Fig. 2b). As expected, a carbonaceous char is left behind after the thermal degradation, with a higher fluorine content especially at 330 °C (ESI Fig. S6†).

The exudates from the thermal degradation were analysed *in situ* using both IR and MS. From the IR data, water vapour and  $\text{CO}_2$  were the two main detected products. This concurs with an earlier study on thermal decomposition of native and oxidized paper, where the main products were observed to be  $\text{CO}_2$  (2400  $\text{cm}^{-1}$ ), CO (1000–1300  $\text{cm}^{-1}$ ) and  $\text{H}_2\text{O}$  (1500  $\text{cm}^{-1}$  and 3500  $\text{cm}^{-1}$ ).<sup>25</sup> In the current study, these are the main observed products, although the CO was also observed as trace by-product which can be attributed to incomplete combustion of the paper. Presence of water vapor is only observed during the first rapid thermal degradation, while in the latter degradation region,  $\text{CO}_2$  is primarily released suggesting that the slow degradation centred at 430 °C could be due to oxidation of C(0) from incomplete combustion in the initial step. The lack of an IR peak broadly spread from 3600–4000  $\text{cm}^{-1}$  suggests that no significant amounts of HF are released irrespective of the paper treatment time.

To further confirm the absence of HF during incineration, mass spectrometry was performed on evolved gases. At 330 °C, the constituents were mostly water ( $m/z = 18$ ) and small portion of  $\text{CO}_2$  ( $m/z = 44$ ) as deduced from the total ion concentration (Fig. 2e). As demonstrated by the IR, at 430 °C  $\text{CO}_2$  was the main

component (Fig. 2f). From the MS, no HF ( $m/z = 20$ ) was observed in either of the two temperatures, which is in agreement with the FTIR analysis. We anticipated that degradation of the polymeric coating would lead to  $\text{CF}_2$  ( $m/z = 50$ ) and CF ( $m/z = 31$ ) signals from the MS, but none were observed. Yet from the collected mass spec even when extending the range to  $m/z$  100 (see ESI†) there was no signal detected implying that the fluoro alkyl tails are not decomposing even at high temperatures.

Temperature-resolved (or time-resolved) 3D FT-IR and 3D mass spectra were also generated (Fig. 3a and b respectively). Fig. 3a shows the FT-IR of evolved gas species over the range of temperature during the incineration of 24 h silane treated paper. Once again,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are the main constituents released from thermal degradation. Temperature-resolved 3D mass spectrum (Fig. 3b) shows significant amounts of CO ( $m/z = 28$ ), which can be attributed to incomplete combustion of the paper. However,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as expected, are the main and dominant products.

### Liquid and solid phase

The solid by-products (ash) of thermally degraded functionalized paper was analyzed *via* energy-dispersive X-ray spectroscopy (EDS) (Fig. S6†). Fluorine was detected when silanized paper was heated until 350 °C, however, above 700 °C the element was absent from the by-product. To track the location

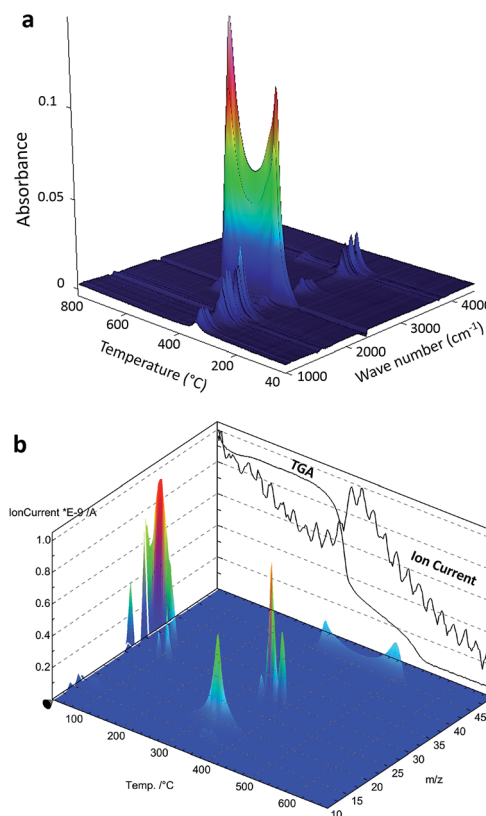


Fig. 3 Temperature-resolved 3D FT-IR (a) and mass spectrometry analysis (b) of high-density paper treated with fluorinated organo-silicon with a reaction time of 24 hours.

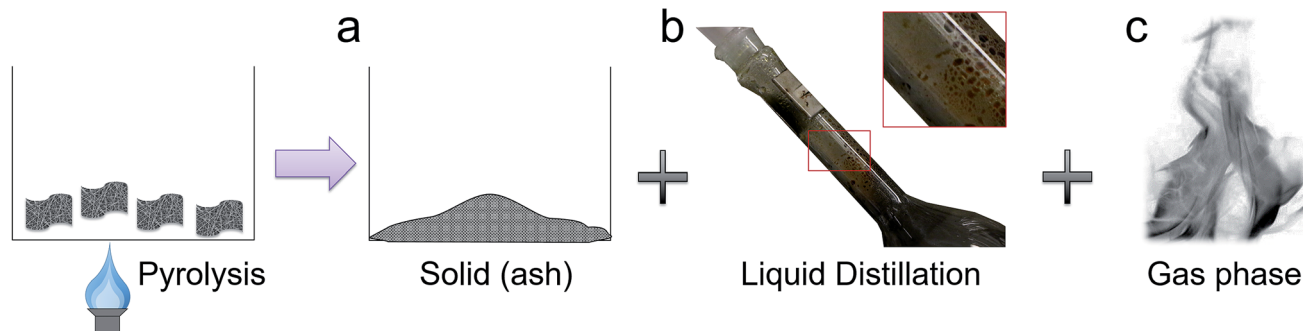


Fig. 4 Study of the phase transformation of the functionalized paper upon heating. Three products were collected from the paper degradation as shown in the schematic; (a) ash residue was analyzed by EDS; (b) distillate was analyzed by NMR and (c) gas phase by-product analyzed by TGA-IR-MS.

of fluorine, silanized paper was heated to temperatures above 700 °C and the evolved products were collected in a distillation column (Fig. 4b). NMR ( $^{19}\text{F}$ ,  $^1\text{H}$  and  $^{13}\text{C}$ ) spectra were collected from the distillate (ESI Fig. S7–S9†). The NMR spectra verifies the presence of fluorine in the distillate, showing that the surface polymer (from silane treatment) distills out of the paper during thermal degradation instead of forming toxic H-F (Table 1).

The use of fluorinated organosilicon reagent for the control of wetting properties of cellulose can be easily performed, in an affordable procedure, as reported.<sup>19</sup> The widespread implementation of hydrophobic paper devices has been limited due to safety concern that originates from the notion that thermal degradation always leads to deleterious effect on human health due to generation of highly toxic HF by-product. This study, however, shows that incineration of cellulose treated with per-fluoro alkyl silane (up to 800 °C) does not generate HF as confirmed by TGA-FTIR-MS and NMR analysis. This work provides evidence that hydrophobic paper treated with organofluorine reagents can safely be disposed by incineration (with concomitant recovery of the perfluorinated reagent), a primary method of waste disposal where proper biomedical waste management is not available. This study informs the adoption and management of paper-based devices especially in developing world, illustrating that controlling the surface modification process enables better recovery of the fluorinated alkyl

chains mitigating environmental contamination or generation of the toxic HF.

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## Notes and references

- 1 T. Liang, C. N. Neumann and T. Ritter, *Angew. Chem., Int. Ed.*, 2013, **52**, 8214–8264.
- 2 R. Fields, R. N. Haszeldine and A. F. Hubbard, *J. Chem. Soc. C*, 1971, 3838–3843.
- 3 S. Mandal, G. Das, S. Dhar, R. M. Tomy, S. Mukhopadhyay, C. Banerjee and A. K. Barua, *Mater. Chem. Phys.*, 2015, **157**, 130–137.
- 4 N. Kiraz, E. Burunkaya, O. Kesmez, M. Asilturk, H. E. Camurlu and E. Arpac, *J. Sol-Gel Sci. Technol.*, 2010, **56**, 157–166.
- 5 E. Burunkaya, N. Kiraz, O. Kesmez, M. Asilturk, H. E. Camurlu and E. Arpac, *J. Sol-Gel Sci. Technol.*, 2010, **56**, 99–106.
- 6 F. L. M. Pattison and R. E. A. Dear, *Can. J. Chem.*, 1963, **41**, 2600–2606.
- 7 Hydrogen Fluoride: MSDS No. 001077, Airgas: Radnor, PA USA; August 7, 2015; <https://www.airgas.com/msds/001077.pdf>; accessed February 14, 2016.
- 8 H. H. Abdullah, A. Z. M. Asa'ari, N. I. M. Zawawi, L. C. Abdullah and S. Zakaria, *BioResources*, 2013, **8**, 4088–4100.
- 9 J.-F. Bloch, P. J. J. Dumont, S. R. du Roscoat, L. Orgeas, C. Geindreau and N. Bouquet, *Mec. Ind.*, 2009, **10**, 43–48.
- 10 D. A. Bruzewicz, M. Reches and G. M. Whitesides, *Anal. Chem.*, 2008, **80**, 3387–3392.

Table 1 Summary of data showing the presence or absence of fluorine at different temperatures in different pyrolysis products. The fluorinated materials are limited to the residue at low temperature but distil off (liquid) at higher temperatures. No detectable fluorine is observed in the gas phase

| Temperature | Presence of fluorine |    |   |
|-------------|----------------------|----|---|
|             | a                    | b  | c |
| 350 °C      | ✓                    | ND | × |
| >700 °C     | ×                    | ✓  | × |

- 11 L. Cai, C. Xu, Y. Chen, M. Zhong and Y. Wu, *Chem. Lett.*, 2015, **44**, 917–919.
- 12 E. Carrilho, A. W. Martinez and G. M. Whitesides, *Anal. Chem.*, 2009, **81**, 7091–7095.
- 13 G. Chitnis, Z. Ding, C.-L. Chang, A. Savran Cagri and B. Ziaie, *Lab Chip*, 2011, **11**, 1161–1165.
- 14 A. C. Glavan, D. C. Christodouleas, B. Mosadegh, D. Yu Hai, B. S. Smith, J. Lessing, T. M. Fernandez-Abedul and G. M. Whitesides, *Anal. Chem.*, 2014, **86**, 11999–12007.
- 15 C. Ververis, K. Georgiou, N. Christodoulakis, P. Santas and R. Santas, *Ind. Crops Prod.*, 2004, **19**, 245–254.
- 16 S. Oyola-Reynoso, A. P. Heim, J. Halbertsma-Black, C. Zhao, I. D. Tevis, S. Çınar, R. Cademartiri, X. Liu, J.-F. Bloch and M. M. Thuo, *Talanta*, 2015, **145**, 73–77.
- 17 S. Oyola-Reynoso, A. P. Heim, J. Halbertsma-Black, C. Zhao, I. D. Tevis, S. Çınar, R. Cademartiri, X. Liu, J.-F. Bloch and M. M. Thuo, *Talanta*, 2015, **144**, 289–293.
- 18 S. Oyola-Reynoso, Z. Wang, J. Chen, S. Çınar, B. Chang and M. Thuo, *Coatings*, 2015, **5**, 1002–1018.
- 19 S. Oyola-Reynoso, I. Tevis, J. Chen, B. S. Chang, S. Cinar, J.-F. Bloch and M. M. Thuo, *J. Mater. Chem. A*, 2016, DOI: 10.1039/c6ta06446a.
- 20 A. C. Glavan, R. V. Martinez, A. B. Subramaniam, H. J. Yoon, R. Nunes, H. Lange, M. M. Thuo and G. M. Whitesides, *Adv. Funct. Mater.*, 2014, **24**, 60–70.
- 21 X. Tian, S. Shaw, K. R. Lind and L. Cademartiri, *Adv. Mater.*, 2016, **28**, 3677–3682.
- 22 V. V. Naik, M. Crobu, N. V. Venkataraman and N. D. Spencer, *J. Phys. Chem. Lett.*, 2013, **4**, 2745–2751.
- 23 V. V. Naik, R. Stadler and N. D. Spencer, *Langmuir*, 2014, **30**, 14824–14831.
- 24 C. R. Robbins and E. M. Levin, *J. Res. Natl. Bur. Stand., Sect. A*, 1961, **65**, 127–131.
- 25 H. Yang, R. Yan, H. Chen, C. Zheng, D. H. Lee and D. T. Liang, *Energy Fuels*, 2006, **20**, 388–393.