

Article

Hydrothermally stable, conformal sulfated zirconia monolayer catalysts for glucose conversion to 5-HMF.

Amin Osatiashtiani, Adam Fraser Lee, Marta Granollers, D. Robert Brown, Luca Olivi, Gabriel Morales, Juan A Melero, and Karen Wilson

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.5b00965 • Publication Date (Web): 02 Jun 2015 Downloaded from http://pubs.acs.org on June 9, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Hydrothermally stable, conformal sulfated zirconia monolayer catalysts for glucose conversion to 5-HMF.

Amin Osatiashtiani^a, Adam F. Lee^a, Marta Granollers^b, D. Robert Brown^b, Luca Olivi^d, Gabriel Morales^c, Juan A. Melero^c, Karen Wilson^a*

^a European Bioenergy Research Institute (EBRI), Aston University, Aston Triangle, Birmingham, B4 7ET, UK

^b Department of Chemical Sciences, University of Huddersfield, Huddersfield, HD1 3DH, UK

^c Department of Chemical and Energy Tech, Chemical and Environmental Tech, Mechanical Tech and Analytical Chemistry,

Universidad Rey Juan Carlos, C/Tulipan. s/n. E-28933, Móstoles, Madrid, Spain

^d Sincrotrone Trieste, AREA Science Park, 34149 Basovizza, Trieste, Italy

ABSTRACT: The grafting and sulfation of zirconia conformal monolayers on SBA-15 to create mesoporous catalysts of tunable solid acid/base character is reported. Conformal zirconia and sulfated zirconia (SZ) materials exhibit both Brönsted and Lewis acidity, with the Brönsted:Lewis acid ratio increasing with film thickness and sulfate content. Grafted zirconia films also exhibit amphoteric character, whose Brönsted:Lewis acid site ratio increases with sulfate loading at the expense of base sites. Bilayer ZrO₂/SBA-15 affords an ordered mesoporous material with a high acid site loading upon sulfation and excellent hydrothermal stability. Catalytic performance of SZ/SBA-15 was explored in the aqueous phase conversion of glucose to 5-HMF, delivering a threefold enhancement in 5-HMF productivity over non-porous SZ counterparts. The co-existence of accessible solid basic/Lewis acid and Brönsted acid sites in grafted SZ/SBA-15 promotes the respective isomerization of glucose to fructose and dehydration of reactively-formed fructose to the desired 5-HMF platform chemical.

KEYWORDS: SBA-15, Sulfated zirconia, Solid acid, 5-HMF, Hydrothermal Stability, Solid Base

1. INTRODUCTION

The quest for sustainable resources to meet the demands of a rapidly rising global population while reducing anthropogenic CO₂ emissions and associated climate change represents one of this century's grand challenges. If average global temperature rises induced by greenhouse gases are not to exceed 2 °C, then estimates indicate that a large proportion of oil, gas and coal reserves must remain untouched.¹ Biomass offers the most readily implemented, and low cost solution for carbon neutral transportation fuels,² and the only non-petroleum route to organic molecules for the manufacture of bulk, fine and speciality chemicals³ and polymers⁴ required to meet future societal demands. 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.⁵ In this respect, lignocellulosic biomass offers great potential for green production of fuels and chemicals.⁶ Among these chemicals, 5hydroxymethylfurfural (5-HMF),⁷ identified by the US DoE^{8,9} as a versatile intermediate for the production of value-added chemicals and high performance liquid fuels, has attracted worldwide attention.10

Aqueous phase, hydrothermal processing of cellulose and sugars offers an attractive method to produce platform chemicals and fuels.¹¹ In a biorefinery, aqueous sugar streams may be produced from lignocellulose via fractionation methods such as steam explosion and enzymatic hydrolysis.¹² The development of heterogeneous catalysts for aqueous phase conversion of such resources requires materials with improved hydrothermal stability.¹³ Furthermore it would be desirable for catalysts to exhibit bifunctional properties such as tuneable acid:base character to initiate cascade reactions in biomass conversion processes.¹⁴ Carbon, zirconia and titania supports¹⁵ are amongst materials reported to exhibit excellent hydrothermal stability and desirable characteristics for application in biomass processing. However, in their native form they exhibit low surface areas, and offer limited control over internal porosity, which restricts their application for the chemical conversion of bulky bio-based molecules.

We reported previously on the aqueous phase conversion of glucose to 5-HMF using a bifunctional sulphated zirconia (SZ) catalyst, in which the amphoteric nature of zirconia was exploited in conjunction with controlled surface sulfation to tune the acid-base properties.¹⁶ Tailoring the acid:base distribution can generate a material with the necessary base sites for glucose—fructose isomerisation, and Brönsted acid sites optimized for the subsequent conversion of reactively-formed fructose to 5-HMF. Although such non-porous zirconias are promising, their intrinsic rate of 5-HMF productivity requires significant enhancement to improve catalyst efficiency and underpin a commercial process. Methods to stabilize highly porous and/or dispersed tunable ZrO_2 and SO_4/ZrO_2 phases are thus required.¹⁷

The direct synthesis of mesoporous ZrO₂ and ZrO₂/SiO₂ has been reported via sol-gel^{18,19,20,21} or co-precipitation methods.^{22,23} However, poor thermal stability and associated pore-collapse during catalyst activation has limited the utility of such templated zirconias.^{24,25} Robust high surface area supports such as nanostructured silicas (e.g. HMS-24,²⁶ MCM-41 and SBA-15) have the potential to serve as high area scaffolds with welldefined mesoporosity over which to disperse ZrO₂, but in order to **Environment**

ACS Paragon Plus Environment

maintain the internal pore network and hence molecular accessibility, it is critical that zirconia is introduced in a layer-by-layer fashion so as to minimise the formation of low area three dimensional crystallites and/or pore blockage. Incipient wetness impregnation,²⁷⁻³² urea hydrolysis³³ and vapor induced hydrolysis (VIH)^{25,34} methods have been reported to prepare ZrO₂ coatings on SBA-15, typically employing zirconium propoxide²⁷⁻³¹ or acetate¹¹ precursors in an anhydrous organic solvent (e.g. dry hexane or 50:50 vol% anhydrous toluene:ethanol). However, simple variation of the precursor concentration to achieve different zirconia loadings invariably yields 3-4 nm crystallites, similar to the silica mesopore diameter. VIH methods employing zirconium oxychloride (ZrOCl₂.8H₂O) or zirconyl nitrate²⁵ precipitation with urea or NH₃/water have succeeded to introduce zirconium hydroxide within SBA-15 mesopores, however attempts to sulphate the resulting zirconia films yield a material prone to S leaching.³

Here we report a synthetic route to high area SZ/SBA-15 catalysts possessing good textural properties and molecular access to in-pore ZrO_2 and SO_4 active sites. The evolution of acid/base properties was explored as a function of the thickness and degree of sulfation of conformal zirconia monolayers (MLs), and the resulting physicochemical properties correlated with catalytic performance in the aqueous phase telescopic conversion of glucose \rightarrow 5-HMF.

2. EXPERIMENTAL

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60

2.1 Catalyst preparation. ZrO₂ grafted SBA-15 was synthesized according to our previous report.³⁵ Briefly, 10 g of SBA-15 (pre-pared via the original method of Zhao et al³⁶) was dried at 300 °C for 4 h, then cooled to 100 °C and added to a solution of 58.5 g of 70 % zirconium propoxide in propanol (Sigma-Aldrich) in 300 ml of anhydrous hexane. The amount of zirconium precursor was calculated based on the number of surface hydroxyl groups on SBA-15 (determined from thermal gravimetric analysis). By working in dry solvent it was hoped that reaction would be confined between surface hydroxyls and zirconium propoxide, favouring conformal monolayer growth over the SBA-15 surface. The reaction mixture was refluxed at 69 °C overnight, filtered and washed three times with hexane to remove any unreacted precursor. The material was subsequently rehydrated in 300 ml deionized water under stirring for 4 h to fully hydrolyze any residual propoxide groups. Finally, the catalyst was filtered and dried at 80 °C overnight. This procedure was repeated to produce SBA-15 coated with a nominal second and third monolayer of zirconia. Sulfation of ZrO₂/SBA-15 materials was achieved via their immersion in aqueous sulphuric acid (10 ml acid solution per g sample, H₂SO₄ concentrations spanning 0.005-0.25M) for 5 h, after which samples were filtered and dried overnight at 80 °C. The resulting materials were activated by calcination at 550 °C in static air for 3 h.

2.2 Catalyst Characterization. N₂ porosimetry was performed on either a Micromeritics TRISTAR 3000 or Quantachrome Nova 4000 porosimeter, with BET surface areas calculated over the range P/P0 = 0.03-0.19, wherein a linear relationship was maintained. Pore size distributions were obtained applying the BJH model to the desorption branch of the isotherm. Structural order was evaluated by means of low angle X-ray powder diffraction (XRD) on a Bruker D8 Advance diffractometer using the Cu K_a line in the range 20 =0.6-5.0 ° with a step size of 0.02°, with phase identification evaluated by wide angle XRD in the range 20=10-80 ° with a step size of 0.04 °. HRTEM measurements were performed on a Philips TECNAI-20T electronic microscope operated at 200 kV. Bulk zirconium contents were determined by scanning electron microscopy (SEM) on a PHILIPS XL 30 ESEM electronic microscope equipped with EDX. X-ray Photoelectron Spectroscopy (XPS) was performed on a Kratos Axis HSi photoelectron spectrometer equipped with a charge neutralizer and Mg K_a X-ray source (hv = 1253.6 eV). Spectra were recorded at normal emission with an analyzer pass energy of 20 eV and X-ray power of 225 W. ZrO₂ film thicknesses were calculated from the attenuation of the Si 2p signal using equation 1:

$$I = I_0 \exp(\frac{-u}{\lambda \cos \theta})$$
 (Equation 1)

where *I* is the peak intensity, I_0 is the intensity of the clean SBA-15 surface, λ is the inelastic mean free path for Si 2p photoelectrons taken to be 1.26 nm, *d* the film thickness and θ the angle of photoelectron emission.^{37,38}

Acid and base site loadings and adsorption enthalpies were determined via adsorption flow calorimetry of NH₃ and SO₂ respectively on a Setaram DSC111 system connected to gas flow and switching systems. Samples were outgassed at 450 °C under flowing N₂ (10 ml.min⁻¹) for 2 h prior to pulse titration at 150 °C. A steady 10 ml.min⁻¹ flow of N₂ was maintained across the sample for 3 h at 150 °C to effect activation. A sequence of 10 probe gas pulses (1 vol% of probe gas in N₂) were delivered to the carrier gas stream from a 2 ml sample loop for NH₃/SO₂ using a twoposition Valco valve with an automated micro-electric actuator. Heat output associated with interaction between the probe gas and the sample was detected by DSC, and the concentration of NH₃/SO₂ in the gas flow downstream of the DSC was measured with a HPR 20 Hiden MS gas analyzer via a heated capillary at 175 °C. The time between pulses was 90 min for NH₃ and 30 min for SO₂ to allow desorption of any reversibly adsorbed probe gas back into the pure N₂ stream, and/or redistribution on the sample, and baseline stabilization. Temperature Programmed Desorption was performed on probe-saturated samples by ramping the temperature from 150-400 °C at 5 °C.min⁻¹.

Ex-situ pyridine adsorption was performed by exposure of diluted samples (10 wt% in KBr) to pyridine vapour overnight. Excess physisorbed pyridine was removed in *vacuo* at 30 °C prior to recording in *vacuo* Diffuse Reflectance Infra-red Fourier Transform (DRIFT) spectra at 50 °C in an environmental cell. Spectra were obtained using a Nicolet Avatar 370 MCT with Smart Collector accessory. Zr K-edge transmission X-ray absorption spectroscopy (XAS) was performed at the XAFS beamline of the Elettra synchrotron with a Si(111) double-crystal monochromator at 250 mA / 2 GeV.

2.3 Catalytic tests. Kinetic studies of glucose (Sigma-Aldrich 99.5%) and fructose (Sigma-Aldrich 99%) conversion were conducted in a Radleys Starfish carousel reactor under stirred batch conditions at 100 °C. Reactions were performed using 0.1 g reactant, 0.1 g catalyst, and 20 ml deionized water. Samples were withdrawn periodically and filtered prior to analysis on an Agilent 1200 series HPLC equipped with Refractive Index and UV diode array detectors, and a Hi-Plex H column. Product yields and selectivity were calculated on a carbon basis according to Equations 2 and 3:

$$\begin{aligned} \textbf{Yield [\%]} &= \frac{(males of C in product)}{(males of C in reactant at t=0)} \times 100 \quad (Equation 2) \\ \\ \textbf{Selectivity [\%]} &= \textbf{Yield} \times \frac{100}{(reactant conversion)} \quad (Equation 3) \end{aligned}$$

Mass balances were determined based on the moles of carbon in the identified products, relative to those in the reactant according to Equation 4: 1

2 3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18 19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59 60

$$\frac{C_{out}}{C_{in}} [\%] = \sum \frac{(moles \text{ of } C \text{ in } product + remaining reactant)}{(mole \text{ of } C \text{ in reactant at } t=0)} \times 100$$
(Equation 4)

Initial reaction rates were determined during the first 3 h, when conversion profiles were linear and <25 %, with resulting activities reported either normalized per mass of catalyst or zirconium. It should be noted low reaction temperatures were selected for this study to minimise background rates for glucose and fructose conversion and facilitate the detailed study of catalyst acid-base properties on activity.

2.4 Hydrothermal stability. The hydrothermal stability of SBA-15 and ZrO_2 /SBA-15 was evaluated in a Parr 5513 autoclave. The reactor was charged with 30 ml deionized water and 0.1 g catalyst, sealed and heated to 170 °C under vigorous stirring for 6 h. Materials were held at this temperature at ~7 bar autogenous pressure, then cooled to room temperature, recovered by filtration and then dried at 80 °C overnight prior to analysis of textural properties by porosimetry and XRD.

3. RESULTS AND DISCUSSION

3.1 ZrO₂ and SZ film growth. The successful stepwise growth of zirconia monolayers over SBA-15 was first verified by a combination of porosimetry, HRTEM, XRD and XPS. Nitrogen porosimetry revealed that all materials exhibited type IV isotherms and steep H1 hysteresis loops typical of mesostructured SBA-15 with a narrow mesopore size distribution (Fig. S3 and S4).³⁹ The composition and textural properties of the parent SBA-15 and ZrO₂ grafted samples are reported in Table S1 and S2 as a function of nominal monolayers of ZrO₂, and are in accordance with our recent communication.ref22 Pore volume, mean mesopore diameter and BET surface area all decreased progressively with each grafting cycle, consistent with a layer-by-layer growth mode of zirconia throughout the mesopore network, resulting in thickening of the mesopore walls and a concomitant reduction of the mesopore diameter. Low angle XRD (Fig S1) also confirmed the mesostructured order of SBA-15 was retained, with materials exhibiting a main peak at $2\theta = -1^{\circ}$ and two weaker features at 2θ = 1.7° and 1.9° attributed respectively to the (100), (110) and (200) reflections of the pmm6 hexagonally ordered parent support.^{36,40} The highly dispersed nature of the incorporated ZrO₂ was verified by the absence of monoclinic or tetragonal phase diffraction features in the wide angle XRD region, indicating dimensions below the instrumental detection limit of around 2 nm. These observations are supported by HRTEM, which visualized an ordered hexagonal SBA-15 mesophase with uniform pore walls following Zr grafting, with no evidence for crystalline zirconia deposits even after three grafting cycles (Fig 1a). Layer-bylayer growth of zirconia overlayers was verified by XPS via attenuation of the Si 2p signal; Fig 1a reveals an exponential decay in the SBA-15 substrate intensity with consecutive zirconia depositions. The first and second grafting cycles attenuated the substrate by 35.6 and 51.9 %, equating to 0.5 and 0.84 nm thick overlayers of ZrO₂ respectively, in excellent agreement with the estimated thicknesses of (111) oriented mono- and bilayers of ZrO₂ (Fig 1b), confirming their conformal nature.

Sulfation of the 1-3 ML ZrO₂/SBA-15 samples was subsequently performed by impregnation with 0.075 M H_2SO_4 (the concentration previously reported to afford optimum acid site properties)¹⁶ and calcination at 550 °C. The absence of any new XRD feastures post-sulfation confirmed the absence of large SZ crystallites. Furthermore, the Zr:Si atomic ratios from XPS and EDX were unchanged by sulfation, suggesting no change in the film morphology from the parent zirconia overlayer (e.g. sulfateinduced sintering).



Fig 1. (a) Attenuation of Si 2p XP signal of $ZrO_2/SBA-15$ as a function of zirconia grafting cycle (dashed line shows the theoretical attenuation predicted from equation 1), inset shows HRTEM of pore channels following 2 and 3 grafting cycles; and (b) Estimated film thickness for 1 and 2 ML ZrO_2 over a SiO₂ substrate.

The bulk and surface S:Zr atomic ratios fell with initial ZrO_2 thickness, indicating only the terminating zirconia layer underwent sulfation (**Table S2**).

Acid site strength, loading and nature was probed by a combination of NH₃ calorimetry and pyridine titration. Fig 2 shows NH₃ pulse calorimetry profiles for SZ/SBA-15, which evidence predominantly moderate strength acidic sites (- ΔH_{ads} ~100-120 kJ.mol⁻¹), comparable to those in bulk SZ catalysts.¹⁶ The 1 and 2 ML SZ/SBA-15 samples also exhibit a small proportion of strong acid sites with $-\Delta H_{ads} \sim 180-200 \text{ kJ.mol}^{-1}$. While the precise origin of these strong acid sites is unclear, they likely originate through the truncated nature of the ZrO₂ monolayers, and corresponding defective (uncoordinated Zr⁴⁺) centres which may confer strong Lewis acidity, being electronically perturbed by the underlying silica.⁴¹ This hypothesis is supported by pyridine titration and quantification of the resultant DRIFT spectra⁴² (Fig 3 and S7) which show a switchover from Lewis to Brönsted acidity with increasing ZrO₂ film thickness. The Zr 3d XP spectra (Fig S5) also exhibits a shift to lower binding energy with increased layer thickness, demonstrating the electron deficient nature of the first layer at the SiO_2 interface. The maximum acid site density (Fig 3) was following sulfation of a zirconia bilayer. Interfacial zirconia thus appears either more chemically inert due to perturbation by the underlying SBA-15 support, or an inability to crystallize in the requisite tetragonal phase known to impart superacidity.⁴³ The acid:base density was independent of zirconia film thickness, being dominated by solid acid character.



Fig 2. NH₃ pulse calorimetry of 1-3 ML SZ/SBA-15.

The highly dispersed nature of the conformal ZrO₂ monolayers prohibited their phase analysis by conventional powder XRD, hence Zr K-edge XAS was performed to inform the structure of both zirconia and SZ films. The common cubic, tetragonal and monoclinic ZrO₂ phases exhibit characteristic XANES spectra, whose lineshape and width are dictated by symmetry-dependent splitting of the 1s→4d transition.^{44,45} Symmetrical cubic ZrO₂ (8coordinate Zr⁴⁺) affords a sharp edge jump and two well resolved transitions to eg and t_{2g} valence states. In contrast, tetragonal (8coordinate Zr⁴⁺) and monoclinic (7-coordinate Zr⁴⁺) phases possess lower symmetry, leading to further splitting of the Zr 4d valence band.



Fig 3. Acid and base properties of 1-3 ML SZ/SBA-15.

Tetragonal ZrO₂ K-edge XANES split into four $(a_1, b_1, e \text{ and } b_2)$ bands which are typically resolved as a doublet, while the monoclinic phase possesses five non-resolvable states observed as a featureless single peak at the white line. Fig 4 shows that the 2 ML ZrO₂/SBA-15 exhibits three distinct features, a weak pre-edge feature labelled A, and a split white line labelled B and C, which are more clearly discerned in the derivative spectra.

Tetragonal ZrO₂ comprises two non-equivalent tetrahedral ZrO₄ units, with different Zr-O bond lengths. Enhanced s-p mixing in tetrahedral geometries^{45,46} gives rise to an extra electronic state ~6-7 eV below the Zr K-edge white line which is unique to tetragonal zirconia, and consistent with peak A, evidencing the presence of tetragonal ZrO2 in both ZrO2/SBA-15 and SZ/SBA-15 materials. Sulfation causes the white line to sharpen, with the lower energy feature B strengthening at the expense of C, indicating a change in electronic structure. The rise in B is consistent with the changes in symmetry and charge distribution of the Zr local environment expected to accompany their covalent binding to SO₄ groups. Fig 4 inset shows the radial distribution functions of ZrO₂ and SZ films, revealing features at 2.0 and 3.3 Å, attributable to Zr-O and Zr-Zr first coordination shells; the weak Zr-Zr shell consistent with the ultra-thin nature of the conformal film which hence lacks the complete nearest neighbour shell present within three-dimensional zirconia crystallites.



Fig 4. Normalized and derivative Zr K-edge XANES of 2 ML ZrO₂/SBA-15 and 2 ML SZ/SBA-15. Inset shows corresponding radial distribution functions from the EXAFS spectra.

3.2 Catalytic activity. The catalytic performance of 1-3 ML SZ/SBA-15 in glucose dehydration to 5-HMF at 100 °C is summarized in **Fig 5**. Activity for glucose conversion and resultant 5-HMF production increases from $1\rightarrow 2$ ML, showing little further change for 3 ML. Glucose conversion to 5-HMF is proposed to proceed via a Lewis acid (or base) catalyzed isomerization to fructose, followed by a Brönsted acid catalyzed dehydration as shown in **Scheme 1**. The catalytic performance mirrors both the total acid site loading and Brönsted:Lewis acid ratio, suggesting that 5-HMF production is rate-limited by the Brönsted acid catalysed dehydration. This postulate is supported by the observed accumulation of fructose during reaction (**Fig. S20**), which re-

flects its slower removal through dehydration relative to production via more rapid glucose isomerisation.



Fig 5. Comparison of activity for glucose conversion and HMF production at as a function of SZ film thickness.



Scheme 1. Glucose isomerization to fructose and subsequent dehydration to 5-HMF.

3.3 Effect of sulfate coverage. Our previous studies of bulk SZ demonstrated that the telescopic glucose \rightarrow fructose \rightarrow 5-HMF reaction could be tuned through controlling the degree of surface sulfation of the underlying amphoteric zirconia, i.e. SO₄ coverage (θ).¹⁶ We hence investigated the impact of θ_{SO4} on the behaviour of the optimal 2 ML ZrO₂/SBA-15 material via impregnation with 0.005-0.25 M H₂SO₄. Low angle XRD and N₂ porosimetry confirmed retention of the parent SBA-15 structure for all acid molarities (**Fig S9** and **S11**), although samples treated with >0.1 M H₂SO₄ induced a slight expansion in the mean mesopore diameter may indicate a small degree of zirconia re-dispersion (**Table 1**). XPS and EDX (**Fig S13** and **S14** and **Table S5** and **S6**) confirmed that the Zr content was constant with rising S loading for [H₂SO₄]

 ≤ 0.05 M, however for [H₂SO₄] ≥ 0.1 M both S and Zr loadings decreased, suggesting corrosion and/or dissolution of the ZrO₂ film. This hypothesis was confirmed by the Zr:Si and S:Si surface atomic ratios, which both fell under aggressive sulfation treatment. SZ films prepared with [H₂SO₄] <0.1 M, with S:Zr <0.18 therefore appear chemically stable. NH₃ and SO₂ pulse calorimetry mapped the evolution of acid and base site loadings with S:Zr atomic ratio for the 2 ML SZ/SBA-15 (Fig S15 and S16 and Table S7); acid sites increased steadily with S content at the expense of base sites, in excellent agreement with previous trends observed for bulk SZ.¹⁶ At S:Zr ratios >0.18 the acid site loading reached a plateau, indicating surface saturation with sulfate species. The mean - ΔH_{ads} (NH₃) of 110 kJ.mol⁻¹ was independent of sulfate coverage, indicating a common, predominantly medium strength acid site, consistent with bulk \hat{SZ} ,¹⁶ while the mean -ΔH_{ads}(SO₂) of 100 kJ.mol⁻¹ for 2 ML ZrO₂/SBA-15 was consistent with values for bulk ZrO2 which possesses weak/medium base sites; typical heats of adsorption for SO₂ span 60 kJ.mol⁻¹ (for SiO₂) to 215 kJ.mol⁻¹ (MgO), hence values for 2 ML SZ/SBA-15 materials of 80-129 kJ.mol⁻¹ evince mild basicity.⁴⁷ The evolution of Brönsted:Lewis acid character with θ_{SO4} was quantified by pyridine titration, and confirmed the expected increase in Brönsted acid character with sulfation (Fig S18).

3.4 Catalytic activity. The performance of xM-SZ/SBA-15 catalysts was subsequently evaluated for 5-HMF production from fructose or glucose. 5-HMF productivity per Zr atom from fructose was directly proportional to the concentration of sulphating solution (i.e. θ_{SO4}) (Fig S21), while in contrast that from glucose exhibited a maximum for $[H_2SO_4] = 0.02$ M, equivalent to an acid:base atomic ratio of approximately 4. These observations are qualitatively consistent with our recent study of fructose conversion over bulk SZ catalysts, and in quantitative agreement with that for glucose conversion wherein maximal 5-HMF productivity was attained for a bulk SZ surface with an identical mix of acid:base character. The rise in 5-HMF production from fructose with surface sulfation can be simply understood in terms of the concomitant increase in Brönsted acidity and hence dehydration activity, whereas glucose conversion to 5-HMF requires a balance of surface base/Lewis acid sites (to drive isomerization to fructose) and Brönsted acid sites (for the subsequent dehydration). Despite similarities in the catalytic behaviour of xM-SZ /SBA-15 and bulk SZ materials, the high area conformal SZ monolayers delivered far superior performance in respect of 5-HMF productivity per Zr atom, being three (two) times more active for glucose (fructose) conversion than bulk SZ analogues (Fig 6).

Table 1. Structure, composition and acid/base properties of 2 ML SZ/SBA-15 as a function of H₂SO₄ molarity

Sample	Atomic S:Zr (XPS)	Surface area / m ² .g ⁻¹	Mesopore diameter / nm	Bulk Zr (EDX) / wt%	Bulk S (EDX) / wt%	Acid site loading / mmol.g ⁻¹	Base site loading / mmol.g ⁻¹
SBA-15	-	850	6.8	0	0		
2 ML ZrO ₂ /SBA-15	-	540	5.4	18.7	0.0	0.233	0.079
0.005M SZ/SBA-15	0.01	550	5.6	20.7	0.0		
0.01M SZ/SBA-15	0.02	538	5.6	19.9	0.0	0.275	0.067
0.025M SZ/SBA-15	0.06	506	5.3	20.0	0.6	0.302	0.039
0.05M SZ/SBA-15	0.13	547	5.3	18.8	1.3	0.34	0.017
0.1M SZ/SBA-15	0.18	542	4.3	16.5	1.5	0.397	0.008
0.17M SZ/SBA-15	0.22	557	5.9	11.8	1.5		
0.25M SZ/SBA-15	0.42	483	6.3	9.5	1.7	0.347	0.002



Fig 6. Zr normalized 5-HMF productivity from glucose and fructose over the optimum bulk SZ and SZ/SBA-15 catalysts. (SZ and SZ/SBA prepared from impregnation with 0.02M H_2SO_4 or 0.1 M H_2SO_4 for glucose or fructose reactions respectively).

This difference may reflect the greater dispersion of the thin film system, and increased Lewis character of the grafted SZ film compared to bulk SZ, and hence improved glucose isomerisation of the former. In this respect, we note that while Lewis acids are claimed to be more selective than strong bases like Ca(OH)₂ or Mg(OH)₂ for glucose—fructose isomerisation⁴⁸ (which promote undesired degradation via reverse aldol reactions⁴⁹), in this work the mild basicity of ZrO₂ seems important in promoting 5-HMF formation at low surface θ_{SO4} . The recyclability of our SZ/SBA-15 materials in glucose conversion to 5-HMF was evaluated for two of the most active catalysts, which were recovered after 6 h reaction, dried and re-calcined. Recycled catalysts retained their activity for glucose dehydration, confirming their robust nature (**Fig S22-23**).

3.5 Hydrothermal stability. Heterogeneous catalysts that possess excellent hydrothermal stability are essential to the development of aqueous phase biomass processing. While the reaction temperatures used in this work were mild, related biomass processes operate between 140-180 °C, a regime wherein ordered mesoporous silicas such as SBA-15 exhibit poor hydrothermal stability,^{36,50-52} hindering their wider utility.⁵³ Since bulk ZrO₂ is considered hydrothermally stable, we speculated that dispersion of zirconia over SBA-15 could improve the support stability in high temperature water. **Fig 7** shows pore size distributions and low angle XRD patterns for as-synthesised and 2 ML ZrO₂/SBA-15 before and after heating in water at 170 °C for 6 h.

The parent SBA-15 underwent pore collapse, evidenced by loss of low angle diffraction features and simultaneous broadening of the pore distribution. The zirconia grafted SBA-15 by contrast retained an ordered pore network with uniform, narrow mesopores. Hence it can be concluded that grafting zirconia is beneficial to hydrothermal stability of the SBA-15 support. Dissolution of amorphous silica has been reported by many research groups⁵⁴⁻⁵⁶, even at room temperature.⁵⁷ While silica dissolution from SBA-15 leads to loss of order and pore expansion, the zirconia film protects the SBA-15 support and the structure of the support remains intact.



Fig 7. BJH pore size distributions before (filled symbols) and after (open symbols) hydrothermal treatment of parent SBA-15
 (●) and 2 ML ZrO₂/SBA-15 (▲). Inset shows low angle XRD of as-prepared and post-hydrothermally treated materials.

4. CONCLUSIONS

A conformal grafting method has been employed to grow ZrO₂ monolayers over a mesoporous SBA-15 framework. XAS, XPS and DRIFTS analysis confirms that subsequent wet impregnation with H₂SO₄ results in highly dispersed sulphated tetragonal zirconia monolayers whose acid site density and Brönsted:Lewis acid site ratio is optimal for a 2 ML SZ film. The acid:base properties of these conformal SZ films can be readily tuned by varying the concentration of the sulphating solution; high [H₂SO₄] favouring Brönsted surface acidity. These 2 ML SZ/SBA-15 catalysts were examined towards the aqueous phase conversion of glucose to 5-HMF, displaying significant per site rate enhancements for 5-HMF production than bulk SZ counterparts under identical reaction conditions. Co-existing basic and Lewis acid sites (associated with zirconia exposed within partially sulphated conformal ZrO₂ films) in SZ/SBA-15 materials promote glucose isomerization to fructose, while Brönsted acid (sulfate) sites direct fructose dehydration to 5-HMF. While the absolute performance of our sulfated Zr-SBA-15 catalysts is not exceptional compared to other processes reported,¹⁰ this reflects our interest in developing a green and sustainable process employing water as the solvent, which is known to afford poorer HMF yields than organic solvents such as DMSO (which facilitate sugar dehydration but is not a practical solvent for large scale application). This rationale for selecting an aqueous solvent is simple; all current biomass pre-treatment routes to sugars, e.g. steam explosion, or enzymatic/chemical (acid or base) cellulose hydrolysis, produce aqueous sugar streams,¹² hence the development of heterogeneous catalysts able to operate in water is essential. It is also important to note that our reaction temperature of 100 °C is significantly lower than most literature reports (>140 °C) in order to minimize unwanted side reactions and humin formation, which is problematic at high temperature and often poorly quantified. The finding that zirconia 1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

monolayers confer excellent hydrothermal stability to SBA-15 suggests that ZrO₂/SBA-15 is a promising support material for more widespread application to aqueous phase reforming.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

Low and wide angle XRD patterns, tables with structural parameters and bulk and surface compositions, N₂ porosimetry isotherms and pore size distribution figures, XP spectra, DRIFT spectra for pyridine titration, SO₂ and NH₃ titration and calorimetry figures, tables of catalytic tests for glucose and fructose dehydration to 5-HMF corresponding reaction profiles, normalized activities and recyclability tests, N₂ porosimetry isotherms and a table of physical properties before and after hydrothermal stability test.

AUTHOR INFORMATION

Corresponding Author

*E-mail: k.wilson@aston.ac.uk.

Notes

The authors declare no competing financial interest.

5. ACKNOWLEDGEMENTS

Financial support from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 604307 is gratefully acknowledged. In addition we are also grateful to the EPSRC for funding under EP/K014676/1 and for the provision of Leadership Fellowship to AFL (EP/G007594/4). KW is grateful to the Royal Society for the award of an Industry Fellowship (IF100206). JAM and GM gratefully acknowledge the "Ministerio de Ciencia e Innovación" of Spain through the project CTQ2011-28216, and the Regional Government of Madrid through the project S2013-MAE-2882. Dr Mark Isaacs is also acknowledged for his assistance with XPS measurements.

REFERENCES

(1)Jakob, M.; Hilaire, J. *Nature* **2015**, *517*, 150-152.

(2)Huber, G. W.; Iborra, S.; Corma, A. *Chemical Reviews* **2006**, *106*, 4044-4098.

(3)Kamm, B. Angewandte Chemie International Edition **2007**, *46*, 5056-5058.

(4)Coombs, J.; Hall, K. *Renewable Energy* **1998**, *15*, 54-59.

(5)Fatih Demirbas, M. *Applied Energy* **2009**, *86, Supplement 1*, S151-S161.

(6)Tuck, C. O.; Pérez, E.; Horváth, I. T.; Sheldon, R. A.; Poliakoff, M. *Science* **2012**, *337*, 695-699.

(7)Dashtban, M.; Gilbert, A.; Fatehi, P. *RSC Advances* **2014**, *4*, 2037-2050.

(8)Bozell, J. J.; Petersen, G. R. *Green Chemistry* **2010**, *12*, 539-554.

(9)Agirrezabal-Telleria, I.; Gandarias, I.; Arias, P. L. *Catalysis Today* **2014**, *234*, 42-58.

(10) van Putten, R.-J.; van der Waal, J. C.; de Jong, E.; Rasrendra, C. B.; Heeres, H. J.; de

Vries, J. G. Chemical Reviews 2013, 113, 1499-1597.

(11) Peterson, A. A.; Vogel, F.; Lachance, R. P.; Froling, M.; Antal, J. M. J.; Tester, J. W. *Energy & Environmental Science* **2008**, *1*, 32-65.

(12) Giang, C.; Osatiashtiani, A.; dos Santos, V.; Lee, A.; Wilson, D.; Waldron, K.; Wilson, K. *Catalysts* **2014**, *4*, 414-426.

(13) Stöcker, M. Angewandte Chemie International Edition **2008**, 47, 9200-9211.

(14) Elmekawy, A. A.; Shiju, N. R.; Rothenberg, G.; Brown, D. R. *Industrial & Engineering Chemistry Research* 2014, 53, 18722-18728.

(15) Serrano-Ruiz, J. C.; Luque, R.; Sepulveda-Escribano, A. *Chemical Society Reviews* **2011**, *40*, 5266-5281.

(16) Osatiashtiani, A.; Lee, A. F.; Brown, D. R.; Melero, J. A.; Morales, G.; Wilson, K. *Catalysis Science & Technology* **2014**, *4*, 333-342.

(17) Grecea, M. L.; Dimian, A. C.; Tanase, S.; Subbiah, V.; Rothenberg, G. *Catalysis Science & Technology* **2012**, *2*, 1500-1506.

(18) Fang, H.; Wan, T.; Shi, W.; Zhang, M. *Journal of Non-Crystalline Solids* **2007**, *353*, 1657-1661.

(19) Wong, M. S.; Huang, H. C.; Ying, J. Y. *Chemistry of Materials* **2002**, *14*, 1961-1973.

(20) Wu, Z.-G.; Zhao, Y.-X.; Liu, D.-S. *Microporous and Mesoporous Materials* **2004**, *68*, 127-132.

(21) Flego, C.; Carluccio, L.; Rizzo, C.; Perego, C. *Catalysis Communications* **2001**, *2*, 43-48.

(22) Infantes-Molina, A.; Mérida-Robles, J.; Maireles-Torres, P.; Finocchio, E.; Busca, G.; Rodríguez-Castellón, E.; Fierro, J. L. G.; Jiménez-López, A. *Microporous and Mesoporous Materials* **2004**, *75*, 23-32.

(23) Bosman, H. J. M.; Kruissink, E. C.; Vanderspoel, J.; Vandenbrink, F. *Journal of Catalysis* **1994**, *148*, 660-672.

(24) Das, S. K.; Bhunia, M. K.; Sinha, A. K.; Bhaumik, A. *The Journal of Physical Chemistry C* **2009**, *113*, 8918-8923.

(25) Krishnan, C. K.; Hayashi, T.; Ogura, M. *Advanced Materials* **2008**, *20*, 2131-2136.

(26) Ecormier, M. A.; Lee, A. F.; Wilson, K. *Microporous and Mesoporous Materials* **2005**, *80*, 301-310.

(27) Zhu, Y.; Jaenicke, S.; Chuah, G. K. *Journal of Catalysis* **2003**, *218*, 396-404.

(28) Katryniok, B.; Paul, S.; Capron, M.; Royer, S.; Lancelot, C.; Jalowiecki-Duhamel, L.; Belliere-Baca, V.; Rey, P.; Dumeignil, F. *Journal* of Materials Chemistry **2011**, *21*, 8159-8168.

(29) Gutiérrez, O. Y.; Fuentes, G. A.; Salcedo, C.; Klimova, T. *Catalysis Today* **2006**, *116*, 485-497.

(30) Zhang, J.; Ma, Z.; Jiao, J.; Yin, H.; Yan, W.; Hagaman, E. W.; Yu, J.; Dai, S. *Microporous and Mesoporous Materials* **2010**, *129*, 200-209.

(31) Thitsartarn, W.; Kawi, S. Industrial & Engineering Chemistry Research 2011, 50, 7857-7865.

(32) Reyes-Carmona, Á.; Moreno-Tost, R.; Mérida-Robles, J.; Santamaría-González, J.; Maireles-Torres, P.; Jiménez-López, A.; Moretti, E.; Lenarda, M.; Rodríguez-Castellón, E. *Adsorption* 2011, *17*, 527-538.

(33) Lanzafame, P.; Temi, D. M.; Perathoner, S.; Spadaro, A. N.; Centi, G. *Catalysis Today* **2012**, *179*, 178-184.

(34) Chang, B.; Fu, J.; Tian, Y.; Dong, X. *Applied Catalysis A: General* **2012**, *437–438*, 149-154.

(35) Morales, G.; Osatiashtiani, A.;
Hernandez, B.; Iglesias, J.; Melero, J. A.;
Paniagua, M.; Robert Brown, D.; Granollers, M.;
Lee, A. F.; Wilson, K. *Chemical Communications*2014, 50, 11742-11745.

(36) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548-552.

(37) Bruce, D. W.; O'Hare, D.; Walton, R. I. Local Structural Characterisation: Inorganic Materials Series; John Wiley & Sons, 2013.

(38) Mitchell, D. F.; Clark, K. B.; Bardwell, J. A.; Lennard, W. N.; Massoumi, G. R.; Mitchell, I. V. *Surface and Interface Analysis* **1994**, *21*, 44-50.

(39) Webb, P.; Orr, C. *Analytical methods in fine particle technology,* ; Norcross: Micromeritics Instrument Corporation, 1997.

(40) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Journal of the American Chemical Society* **1998**, *120*, 6024-6036.

(41) Dondur, V.; Rakic, V.; Damjanovic, L.; Auroux, A. J. Serb. Chem. Soc. 2005, 70, 457-474. (42) Emeis, C. A. Journal of Catalysis 1993, 141, 347-354.

(43) Morterra, C.; Cerrato, G.; Signoretto, M. *Catal. Lett.* **1996**, *41*, 101-109.

(44) Yamamoto, T. *X-Ray Spectrometry* **2008**, *37*, 572-584.

(45) Li, P.; Chen, I. W.; Penner-Hahn, J. E. *Physical Review B* **1993**, *48*, 10063-10073.

(46) Mountjoy, G.; Anderson, R.; Newport, R. J.; Smith, M. E. *Journal of Physics: Condensed Matter* **2000**, *12*, 3505.

(47) Ono, Y.; Hattori, H. Solid Base Catalysis,; Springer-Verlag Berlin Heidelberg, 2011; Vol. 101.

(48) Moliner, M.; Román-Leshkov, Y.; Davis, M. E. Proceedings of the National Academy of Sciences of the United States of America **2010**, 107, 6164-6168.

(49) Yang, B. Y.; Montgomery, R. *Carbohydrate Research* **1996**, *280*, 27-45.

(50) Chen, C.-Y.; Li, H.-X.; Davis, M. E. *Microporous Materials* **1993**, *2*, 17-26.

(51) Kim, S. S.; Zhang, W.; Pinnavaia, T. J. *Science* **1998**, *282*, 1302-1305.

(52) Ryoo, R.; Kim, J. M. Journal of the Chemical Society, Chemical Communications **1995**, 711-712.

(53) Liu, Y.; Pinnavaia, T. J. *Journal of Materials Chemistry* **2002**, *12*, 3179-3190.

(54) Okamoto, G.; Okura, T.; Goto, K. *Geochimica et Cosmochimica Acta* **1957**, *12*, 123-132.

(55) Alexander, G. B.; Heston, W. M.; Iler, R. K. *The Journal of Physical Chemistry* **1954**, *58*, 453-455.

(56) Fournier, R. O.; Rowe, J. J. Am. Mineral.; (United States) 1977, 62.

(57) Morey, G. W.; Fournier, R. O.; Rowe, J. J. Journal of Geophysical Research **1964**, 69, 1995-2002.



254x190mm (96 x 96 DPI)