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1. Introduction

One of the biggest challenges in the 21st century is to transition from a fossil-based economy to one based on renewable resources that, besides solar and wind, should include biomass, the most abundant available raw material in nature.^{1,2} Agricultural waste products especially those of lignocellulosic nature from plants such as stalks, wood, kernels and straws are precious renewable biomass feedstocks that are still underexploited.^{3,4} The chemical structures in their existing

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Flame-made amorphous solid acids with tunable acidity for the aqueous conversion of glucose to levulinic acid[†]

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Solid acids of amorphous silica-alumina (a-SA) and amorphous silica-alumina-phosphate (a-SAPO) were prepared by flame spray pyrolysis (FSP). Careful tuning of the acidity of the solid acids was enabled by capitalizing on the advantage of FSP in preserving the metal stoichiometry (*i.e.*, Si, Al, P) in the product nanoparticles. Although the amount of acids on these non-porous solid acids is an order of magnitude lower than the well-recognized strong acidic ZSM-5 zeolite, both exhibit comparable acid strengths. The a-SA and a-SAPO were characterized by a mixture of Brønsted (B) and Lewis (L) acids, and the B/L ratios were composition-tunable. The highest B/L ratios were recorded for a-SA (Al/(Al + Si) = 0.4) and a-SAPO (Si/(P + Si) = 0.25), giving the highest yields of levulinic acid (\geq 40% carbon yield) from the conversion of glucose in the aqueous phase without requiring the addition of liquid acids or metal halides. Under the same conditions, the almost exclusive Brønsted acid ZSM-5 yielded only 17% levulinic acid. The FSP-made solid acid catalyst exhibited good reusability over at least 4 consecutive runs.

forms make it difficult to yield fuels of high calorific values, or value-added chemicals of high quality. Therefore, they need to be broken down into monosaccharide units such as glucose and fructose that can be further converted into a series of robust platform chemicals. Among them, levulinic acid (LA) is listed as one of the top twelve most promising building block chemicals as compiled by the US Department of Energy.⁵

A wide range of valuable commodity chemicals can indeed be derived from LA for use as fuel additives, pharmaceuticals, fragrances and plasticizers.⁶ For example, the hydrogenation of LA produces y-valerolactone for use in biofuel-gasoline blends or as a general solvent for lacquers, adhesives and insecticides; the conversion to methyl tetrahydrofuran (via 1,4pentanediol) for use as fuel blends and as monomers for polymer fibers; the esterification of LA to levulinic ester as a diesel additive; and the condensation of LA with esters to produce α -methylene- γ -valerolactone, new а acrvlic monomer.4,6 Traditionally, the conversion of glucose or fructose to LA is catalyzed by liquid Brønsted acids such as HCl, H₂SO₄, and H₃PO₄, in combination with Lewis acids in the form of metal chlorides (e.g., CrCl₃, AlCl₃, CuCl₂, FeCl₃), where the standard has been to use the toxic CrCl₃.⁷ The reaction is well-established to consist of three sequential steps, namely, the isomerization of glucose to fructose, the dehydration of fructose to 5-hydroxymethylfurfural (5-HMF), and the rehydration of 5-HMF to LA and formic acid (FA) (Scheme 1).⁷⁻⁹ The decompositions of glucose, fructose and 5-HMF also occur in

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parallel, leading to the formation of humins as byproducts. In these sequential reactions, mixed Brønsted and Lewis acids are often necessary to achieve high LA yields. Prior studies suggested that Lewis acids promote the isomerization of glucose to fructose,¹⁰ while the combination of both types of acids is typically required for the fructose dehydration and its further rehydration to LA.^{11,12}

Compared with liquid acids, solid acid catalysts are advantageous as they are easier to handle, non-corrosive, readily separable from the end liquid or gas products, and hence easily recyclable.^{13,14} For that reason, a wide range of solid acids and their modifications were developed and shown to be effective in catalysing various biomass-related conversions.15-18 Of particular interest, the ZSM-5 aluminosilicate zeolite is a popular standalone solid acid catalyst for the production of LA, albeit without requiring the addition of metal halides as homogeneous phase Lewis acids.¹⁹ Other solid acids such as metal (IV) phosphates have also been demonstrated as standalone catalysts for the aqueous-phase conversion of glucose to HMF and LA.^{20,21} These are much cheaper alternatives compared with ion-exchange polymer resins such as Amberlyst and Nafion, with reported LA yields of 28 and 40% (with addition of 0.2 M H₂SO₄), respectively.^{21,22}

In this paper, we report the rapid synthesis of amorphous silica-alumina (a-SA) and amorphous silica-alumina-phosphate (a-SAPO) solid acids by flame spray pyrolysis (FSP) as promising alternative catalysts for the aqueous conversion of glucose to LA. FSP is an industrially-relevant and scalable process capable of producing high quality, size-tunable nanoparticles in the order of kilograms per hour at the pilot scale.²³⁻²⁵ Another major advantage of FSP is the ability to fully preserve the metal stoichiometry in the final product catalyst nanoparticles.^{26,27} As will be demonstrated in the current work, such precise control over the stoichiometry of the product is pivotal in the design of solid acids, since the amount of acid is dictated by the amount of Al³⁺ substitution in Si^{4+} in the case of a-SA, and the Si^{4+} substitution in P^{5+} in the case of a-SAPO, respectively. Systematic variation of these substituents and thorough characterization allow insights into their acidic characteristic-activity relationships of the resultant flame-made solid acids. Comparison is also made between the

non-porous flame-made solid acids and the microporous ZSM-5 zeolite, showing a more than 2-fold increase in LA yield in the former. To the best of our knowledge, this work is the first to demonstrate ready-to-use, FSP-made catalysts for glucose conversion.

2. Experimental

2.1. Flame synthesis and characterization of solid acids

The liquid precursor for the synthesis of a-SA series solid acids was composed of an appropriate amount of tetraethyl orthosilicate (TEOS, 98%, Aldrich) and aluminium tri-secbutoxide (97%, Acros) codissolved in xylene. The total concentration of Al + Si was kept constant at 0.5 M. In the case of a-SAPO, the concentration of aluminium tri-secbutoxide (97%, Acros) was fixed at 0.25 M and appropriate amounts of tributyl phosphate (99%, Aldrich) and TEOS were dissolved in xylene to give a combined Al + Si + P concentration of 0.5 M. All liquid precursors were prepared in a N₂-filled glovebox. During FSP,²⁸ the liquid precursor was fed at a rate of 5 or 1 mL min⁻¹ using a syringe pump. At the FSP nozzle tip, the liquid precursor was dispersed by 5 L min⁻¹ O₂ (1.5 bar) and ignited by a surrounding oxy-methane supporting flame (1.5 L min⁻¹ $CH_4/3.2$ L $\min^{-1} O_2$) to form the primary aerosol flame. Additional 5 L \min^{-1} of sheath O₂ was issued through the outermost stainless steel ring consisting of 12 equally spaced outlets (0.8 mm diameter). The product particles leaving the primary flame were collected on a glassfibre filter (Whatmann GF/D) with the aid of a vacuum pump (Edwards). Commercial ZSM-5 zeolite (CBV 2314) and Zeolite X were purchased from Zeolyst International and Grace Davison, respectively.

The X-ray diffraction (XRD) of the as-prepared catalysts was measured on a PANalytical X'Pert3 diffractometer equipped with a PIXCel 1D detector. Cu K α was used as the radiation source operating at 40 kV and 40 mA. The sample was scanned at 0.1° s⁻¹ with a step size of 0.013°. The morphologies of samples were investigated by using a JEM 2200FS transmission electron microscope (TEM) under 200 kV accelerating voltage, and the TEM specimens were prepared by a standard particle preparation protocol: the

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ethanol/particle suspension was dispersed onto a TEM copper grid with a lacey carbon film after sonication for 30 min. The surface elemental compositions of the asprepared samples were characterized by X-ray photoelectron spectroscopy (XPS) on an ESCALab220Xi (Thermo Scientific) using monochromated Al K α (20 eV pass energy) radiation source. Samples were measured under ultrahigh vacuum at $<2 \times 10^{-9}$ mbar. The specific surface area (SSA) of samples was evaluated by nitrogen adsorption at 77 K, using the BET method and measured on a Micromeritics Tristar 3000. Prior to the measurement, the as-prepared samples were evacuated in a Micromeritics VacPrep unit heated to 150 °C for at least 2 h to remove adsorbed moisture and volatile organics. The SSA-equivalent diameter was estimated based on d_{SSA} = $6/(\rho \times SSA)$, where ρ is the mass-weighted density of the sample assuming elementary oxide forms. Ammonia temperature-programmed desorption (NH3-TPD) studies were carried out on a Micromeritics AutoChem 2950 HP chemisorption analyzer equipped with a quadrupole Microstar mass spectrometer. Accurately weighed 0.25 g of the pelletized catalyst was supported on quartz wool plug in a quartz U-tube. The catalysts were pretreated at 400 °C (10 °C min⁻¹) for 1 h under 50 mL min⁻¹ of 5% O₂/He to remove surface carbon residues, and subsequently cooled to 50 °C. The catalyst was surface saturated with NH₃ by flowing 50 mL min⁻¹ of 5% NH₃/He for 1 h. Physisorbed ammonia was removed by switching to He at the same flow rate, flowing for at least 1 h until no change in the thermal conductivity could be measured at the outlet gas. The TPD commences by heating the sample at 10 °C min⁻¹ up to 800 °C and the sample was held at that temperature for an additional 20 min. The desorption products for NH₃ (m/z = 16 and 17), H₂O (m/z = 18) and O_2 (m/z = 32) were monitored by using the mass spectrometer.

Pyridine-adsorbed Fourier-transform infrared (pyridine-FTIR) analyses were carried out in a commercial transmission IR cell (Dewar Transmission/Reflection Accessory, Harrick Scientific) mounted on an FT-IR spectrometer (Vertex 70, Bruker) under N2 purge. To avoid high IR light absorption in the region of interest by the sample itself and achieve good sample homogeneity, a two-step pelletization procedure was employed. First, 200 mg of dried KBr powder was pressed at 5 ton for 5 min and shaped into a round disk of 13 mm diameter. Afterwards 6 mg of a powder sample was homogeneously placed over the KBr disk for further pressing at 1.5 ton for 1 min. In this way, the KBr disk functioned as the support without interacting chemically with the sample. The pelletized sample was placed in the cell, heated to 150 °C, and kept at that temperature for 2 h under vacuum (ca. 5 Pa) and a background spectrum was recorded. Subsequently, 2500 Pa of pyridine was dosed in the cell and stabilized for 30 min. Finally, the cell was evacuated to 5 Pa to remove gaseous and physisorbed pyridine, and the spectrum of chemisorbed pyridine on the sample was also recorded at 150 °C. Each spectrum was measured for 15 min at a resolution of 2 cm⁻¹ using a DTGS detector. The amount of Brønsted (B) and Lewis (L) acid sites

$$C(\mathbf{B},\mathbf{L}) = \mathbf{IMEC}(\mathbf{B},\mathbf{L})^{-1} \times \mathbf{IA}(\mathbf{B},\mathbf{L}) \times \frac{\pi R^2}{W}$$
(1)

where *C* is the concentration of acid sites (μ mol g_{cat}⁻¹), IMEC (B, L) is the integrated molar extinction coefficient (B = 1.67, L = 2.22 cm μ mol⁻¹), IA (B, L) is the integrated absorbance (cm⁻¹), *R* is the radius of the catalyst disk (cm) and *W* is the weight of the catalyst (mg).

2.2. Catalyst assessment

The hydrothermal conversion of glucose to levulinic acid was carried out in a Teflon-lined stainless-steel reactor with a total volume of about 10 ml. D-Glucose (≥99.5%, Aldrich), D-fructose (99%, Alfa Aesar) or 5-hydroxymethylfurfural (\geq 99%, Aldrich) was dissolved in deionized water (18.2 MΩ, Milli-Q). The accurately weighed as-prepared catalyst (5 mg) was suspended in 6 mL of the solution in a reactor and pressurized to 20 bar Ar. The insulated reactor was heated to the target temperature using a stirrer-hot plate (IKA) under magnetic stirring at 600 rpm. To quench the reaction, the reactor was immediately cooled under cold running tap water. Prior to analyses, the suspension was filtered (Pall syringe filter, 0.2 µm nylon). The filtered sample was analyzed on a high performance liquid chromatograph (HPLC, Acquity, Waters) equipped with an Aminex HPX-87H column (50 °C), a photodiode array (210 nm, PDA, Waters) and refractive index (RI, Waters) detectors. The sample (2.5 µL) was eluted using 5 mM H₂SO₄ (98%, HPLC grade, Aldrich) aqueous solution at a flow rate of 0.6 ml min $^{-1}$. The conversion of reactants and product carbon yields are defined in eqn (2) and (3), respectively:

$$Conversion = \frac{[Reactant]_i - [Reactant]_f}{[Reactant]_i} \times 100\%$$
(2)
Yield =
$$\frac{[Product] \times No. \text{ of carbon in the product molecule}}{[Reactant]_i \times No. \text{ of carbon in the reactant molecule}} \times 100\%$$

(3)

where subscripts i and f refer to the initial and final states of the reaction, respectively.

3. Results and discussion

3.1. Physicochemical characteristics of a-SA and a-SAPO solid acids

Amorphous silica-alumina (a-SA) solid acids with different Al/ (Al + Si) molar ratios, ranging from 0 (pure SiO₂), 0.2, 0.4, 0.6, 0.8 to 1.0 (pure Al₂O₃), were synthesized using the one-step FSP. For brevity, the samples are labelled a-SA*x*, where *x* refers to the Al/(Al + Si) percentage molar ratio. It is presented in such a way since Al is the source of acid, and the total amount of Al and Si is kept constant in all a-SA samples. As shown from the X-ray diffraction (XRD) spectra in Fig. 1a, except for the pure



Fig. 1 High resolution XRD spectra of (a) a-SA and (b) a-SAPO series of flame-made solid acids with different compositions. Samples are labelled a-SAx and a-SAPOy, where x and y represent the percentage molar ratios of Al/(Al + Si) and Si/(Si + P), respectively. The XRD peaks are labelled α -Al₂O₃ (open circle, ICSD: 068591), γ -Al₂O₃ (open square, ICSD: 068771) and AlPO₄ (open diamond, ICSD: 71435).

Al₂O₃, which is composed of mixed α - (2 θ = 28.7 and 56.2°) and γ -Al₂O₃ phases (2 θ = 32.5, 36.8, 39.5, 45.9, 61.3 and 67°), all Si-containing samples were predominantly amorphous as reflected by the broad amorphous hump $(2\theta = 17-40^\circ)$. Although the FSP generally produces highly crystalline nanoparticles as a result of the high temperature synthesis (with the highest temperature point reaching up to 2800 K),²⁵ SiO₂ and related composites have been one of the few exceptions,³⁰⁻³² where the typically short flame residence time (in the range of milliseconds) is insufficient to promote the crystallization to quartz. Furthermore, the presence of SiO₂ disrupted the long-range order of the Al₂O₃ unit cells and thus distorted the overall crystallite structure, as evidenced from the broadening and disappearance of Al₂O₃ diffraction peaks with increasing SiO₂ content for a-SA20 and above. Only trace α -Al₂O₃ clusters could be observed under high resolution XRD.

Similar synthesis was carried out to produce amorphous silica-alumina-phosphate (a-SAPOy) solid acids, where y denotes the Si/(P + Si) percentage molar ratio as analogous to the denotation used for a-SA. Here, the total amount of P and Si is kept constant and in equimolar with Al in all a-SAPO samples. The molar ratios of a-SAPO were varied from Si/(P + Si) of 0 (AlPO₄), 0.25, 0.40, 0.67, 0.80 to 1.0 (equivalent to a-SA50). As shown from the XRD in Fig. 1b, in the absence of Si, *i.e.*, a-SAPO0, the monoclinic aluminophosphate (AlPO₄) diffraction peaks could be measured in coexistence with a largely amorphous phase. As in the case of the a-SA series discussed above, the addition of Si disrupted the orderly arrangement of the AlPO₄ unit cells thereby resulting in the formation of fully amorphous solid acids. Because of the high temperature and oxygen-rich flame synthesis, all hydrocarbon components present in the precursors were fully combusted and yielded pristine a-SA and a-SAPO solid acids in their as-prepared forms (see Table S1[†]).

Type II N_2 adsorption-desorption isotherms were measured for all a-SA and a-SAPO samples (Fig. 2), suggesting nonporous morphologies that are characteristic of flame-made

particles. Any surface pores that may form during the flame synthesis would collapse and sinter due to the high temperature environment.^{33,34} Small addition of Al in a-SA increased the specific surface area (SSA) up to 407 m² g_{cat}^{-1} (for a-SA20), beyond which the SSA gradually decreased (Fig. 2b). This corresponds to an initial decrease in the SSA-equivalent diameter, d_{SSA} , from 7 nm for a-SA0 to 5 nm for a-SA20 and followed by the systematic increase up to 9 nm for the pure Al₂O₃. The increase in SSA with an initial small addition of the external element, in this case Al, is commonly observed for flame-made catalysts, e.g., Al₂O₃/Ce_{0.5}Zr_{0.5}O₂³⁵ and Fe₂O₃/ TiO2.²⁷ This lies within the narrow concentration region at which dopants can stabilize the primary particles under the high temperature flame synthesis, but when excess dopants are present this leads to severe sintering and coalescence. In the case of a-SAPO, the increase in the Si content systematically increases the SSA from 58 m² g⁻¹ for pure AlPO₄ to 268 m² g⁻¹ for a-SAPO100, or equivalent to a decrease in d_{SSA} from 34 to 6 nm, respectively (Fig. 2d). A high Si content appears beneficial in attaining a high SSA for both cases of a-SA and a-SAPO, inferring suppressed aerosol coalescence during the FSP.

By reducing the parametric liquid precursor feed flow rate during the FSP synthesis from 5 to 1 ml min⁻¹, this directly decreased the rate of combustion enthalpy resulting in an aerosol flame that is cooler with shorter residence time and lower metal concentrations. Consequently, a smaller particle size (4 nm) and much higher surface area (478 m² g_{cat}⁻¹) were obtained for a-SA40(HSA – high surface area) compared with those of the standard a-SA40 (7 nm, 258 m² g_{cat}⁻¹) (Fig. 2b). *Note*: As will be shown below, the increase in SSA was able to increase the amount of surface acid sites in the former but preserve the surface acid densities in both cases.

Fig. 3a and b contain transmission electron microscopy (TEM) images of the a-SA40 as a representative sample of the a-SA series showing the amorphous nature of the nano-



Fig. 2 Nitrogen adsorption-desorption isotherms of (a) a-SA and (c) a-SAPO of different compositions, and (b and d) their corresponding specific surface area (SSA, solid symbols) and SSA-equivalent diameter (d_{SSA} , open symbols). The a-SA40(HSA) is represented as a triangle in (b).



Fig. 3 TEM images of (a and b) a-SA40 and (c and d) a-SAPO25 and their corresponding electron diffraction pattern (inset), which are diffuse, indicating a predominantly amorphous nature. Also shown in (e and f) are the TEM images of the ZSM-5 zeolite with well-defined channel pores.

particles, as reflected from the diffused electron diffraction pattern. Some necking occurs between the particles, which is typical of silica-rich particles as a result of the gelation in the flame. The TEM images of the representative a-SAPO25 (Fig. 3c and d) show similar morphologies to that of the a-SA, again displaying a predominantly amorphous nature. In contrast, the TEM images of the ZSM-5 zeolite with well-defined channel pores are shown in Fig. 3e and f.

Fig. 4a shows the XPS-determined surface Al/(Al + Si) molar ratio against that of the bulk. A slight decrease in the surface



Fig. 4 XPS-determined surface Al/(Al + Si) or Si/(P + Si) compositions on (a) a-SA and (b) a-SAPO, respectively, as a function of their bulk compositions. The a-SA40(HSA) and ZSM-5 are represented in (a) as an open triangle and square, respectively.

Al for a-SA with mixed compositions can be observed, which is consistent with the slight clustering of Al_2O_3 as seen earlier from the XRD. Clustering of dopants (as oxide) at high concentrations is a way of reducing the overall surface energy of the particles, seen previously for examples in the FSP-made Fe₂O₃/ TiO₂²⁷ and Co₃O₄/ZrO₂.^{36,37} High homogeneity between the surface and bulk Si/(P + Si) ratios was measured for the a-SAPO series in the absence of crystallite clusters, as expected for fully amorphous samples (Fig. 4b). Analysis by XPS confirms the exclusive presence of Si⁴⁺ and Al³⁺ metal ions for a-SA, and additional P⁵⁺ for a-SAPO. As such, we can expect the formation of surface acid sites in accordance with the principles of substitutional doping and charge balance as mentioned earlier.

The amount of surface acid sites was measured using the temperature-programmed desorption of ammonia (NH₃-TPD). As shown in Fig. 5, the NH₃-TPD profiles could be deconvoluted into a series of Gaussian peaks. For each Gaussian peak, it is assumed that (1) the activation energy of NH₃ desorption $(E_{\rm d})$ is constant and independent of NH₃ surface coverage, and (2) a normal distribution of E_d to take into account of the heterogeneity of acid sites distribution.³⁸ It should be noted that m/z 16 (Fig. S1a[†]) was used to monitor desorption of NH₃ instead of the stronger signal m/z 17 (Fig. S1b[†]), which overlaps with fragments from desorbed H_2O (*m*/*z* 18, Fig. S1c[†]). To further confirm that the recorded m/z 16 signal was mainly from the desorption of NH₃ and not from the fragmentation of O_2 or H_2O , the base peaks of H_2O and that of O_2 (*m*/*z* 32, Fig. S1d[†]) show no correlation with the signal at m/z 16. In Fig. 5a and d, the peaks in the low temperature region ($T_{des} <$ 250 °C) are typically composed of a mixture of very weak acid sites irrelevant to chemical reactions and those from desorbed NH₃ hydrogen-bonded to NH₄⁺ on strong Brønsted acid sites, *i.e.*, $NH_4^+ \cdot nNH_3$ $(n \ge 1)$.^{39,40} As such, only NH_3 desorption peaks above 250 °C will be quantified, categorizing them as weak (250 °C \leq $T_{\rm des}$ < 350 °C) and strong acid sites ($T_{\rm des} \geq$ 350 °C). As shown in Fig. 5b, while the amount of weak acid sites for the a-SA series is similar across various compositions, the highest amount of strong acid was measured on a-SA40 $(0.29 \text{ mmol g}^{-1})$ despite being an order of magnitude lower than that of the reference ZSM-5 zeolite (1.5 mmol g^{-1}). The

highly ordered arrangement of the SiO₄ and AlO₄ tetrahedra units and microporous morphology in ZSM-5 afforded an extremely high SSA (419 m² g⁻¹) as well as a high amount of framework Brønsted acid sites (Fig. 3). In contrast, the a-SA solid acids were non-porous and almost completely amorphous. For this reason, the increase in the surface area from a-SA40 to a-SA40(HSA) enhanced the amount of strong acid proportionally (Fig. 5b). It is interesting to note from the T_{des} peaks that the strength of the strong acid components on the flame-made solid acids appear to match those of ZSM-5, corroborating the ¹H and ¹³C MAS NMR measurements by Huang *et al.*⁴¹

To compare the surface quality of the solid acids, their acid contents were normalized to their respective SSA values. As shown in Fig. 5c, the surface density of strong acid sites for a-SA40 (1.1μ mol m⁻²) remains the highest among the a-SA series, consistent with the trend seen earlier based on the gravimetric contents. Similar surface acid densities were measured for both the a-SA40 and a-SA40(HSA). This confirms that the surface acid density can be easily reproduced for FSPmade catalysts of different SSA as long as the bulk composition is retained. The surface density of strong acids on ZSM-5 remained higher than the flame-made solid acids due to the orderly arrangement of the tetrahedra units.

As shown in Fig. 5d and e, the pristine $AIPO_4$ (*i.e.*, sample a-SAPO0) shows a minimum amount of surface acid, but it gradually increases with increasing Si content up to Si/(P + Si) = 0.67 (*i.e.*, sample a-SAPO67). This is augmented in part by the increase in the SSA that scales proportionally to the increase in Si content. However, the optimum composition is shifted to a-SAPO40 when reported as surface acid density (Fig. 5f). Unlike the a-SA series, where significant clustering Al_2O_3 was measured, the a-SAPO was characterized by a more homogeneous surface and bulk amorphous nature. This partially accounts for the multiple-fold increase in acid contents for the a-SAPO catalysts when compared with the a-SA catalysts, based on both the gravimetric content and surface acid densities.

Fig. 6a and c show the FTIR-pyridine spectra of the a-SA and a-SAPO, respectively. In the case of a-SAO, the absorbance



Fig. 5 NH₃-TPD profiles of (a) a-SA and (c) a-SAPO of different compositions, and (b and e) their estimated acid sites normalized to the weight as well as (c and f) that normalized to the surface area of the solid acids. The a-SA40(HSA) and ZSM-5 (Al/(Si + Al) = 0.08) are represented as an open triangle and square, respectively. The deconvoluted peaks in (a and d) are labelled in red (weak acid) and blue (strong acid), while the very weakly adsorbed NH₃ irrelevant to reaction is labelled in grey dashed lines (see the text for details).



Fig. 6 FTIR-pyridine spectra of (a) a-SA and (c) a-SAPO of different compositions, and (b and d) their corresponding ratio of Brønsted-to-Lewis acid sites. The a-SA40(HSA) and ZSM-5 (Al/(Si + Al) = 0.08) are represented in (b) as an open triangle and square, respectively.

band at 1445 cm⁻¹ originates from pyridine hydrogen-bonded to silanol, instead of Lewis sites.²⁹ Likewise, the absorbance band at 1446 cm⁻¹ for a-SAPO0 is attributed to pyridine hydrogen-bonded to surface P-OH. With the exception of these irrelevant bands, the Brønsted and Lewis acid sites can be readily distinguished by the unique absorbance bands at 1543 cm⁻¹ and 1453 cm⁻¹, respectively.⁴² Quantification of the acid sites was carried out based on the extinction coefficients reported by Emeis²⁹ and the ratio of Brønsted-to-Lewis acid sites (B/L) presented in Fig. 6b and d. The highest B/L was measured for a-SA40 (B/L = 1.9), which as discussed earlier also has the highest surface density of acid. The presence of mixed Brønsted and Lewis acids in a-SA is due to the retention of Lewis acids on some of the surface alumina sites, i.e., Si-O…Al. The ZSM-5, on the other hand, is structurally dissimilar from a-SA in that the acid sites in the former are predominantly formed on the bridged Si-O-Al that give rise to almost exclusively Brønsted acids.43 The highest B/L was measured for a-SAPO25 (B/L = 14, Fig. 6d). The variability in the amount of acids as well as the B/L content in the flame-made solid acids provides a suitable avenue for studying their influence on the glucose conversion as well as the LA selectivity.

3.2. Glucose conversions over a-SA and a-SAPO solid acids

Fig. 7 shows the assessment of the a-SA and a-SAPO series catalysts for the hydrothermal conversion of glucose at 180 °C and 24 h, where complete conversion was achieved in all cases. An optimum LA yield of 40% was measured for a-SA40, while a similar optimum yield of 42% was measured for a-SAPO25. The optimum yields coincide with the highest B/L for these two samples within the a-SA and a-SAPO series, respectively. It is interesting to note that despite the increased amount of acid content on the higher surface area analogue of a-SA40(HSA), the LA yield is not higher than that of the standard a-SA40. It implies that the amount of acid is not a limiting factor in the current measurement. In fact, while the mutual existence of both Brønsted and Lewis acids is crucial in both the dehydration of fructose to 5-HMF and further rehydration to LA (Scheme 1), the latter is strongly influenced by the presence of hydronium ions and this is predominantly regulated by Brønsted acid.^{20,44} The ZSM-5 zeolite, which represents a sample with an extremely high amount of almost exclusive Brønsted acid, only resulted in 17% LA yield. The result is consistent with Acharjee and Lee who carried out reactions under similar hydrothermal conditions.¹² Further comparison with commercial Zeolite X, which has the same Si/Al composition as a-SA40, found only 21% LA yield (see Fig. S2†). The a-SA100 or pristine Al₂O₃, which is an almost exclusive Lewis acid, resulted in a low LA yield of 19%. All of the results above reaffirm the importance of mixed Brønsted and Lewis acids for the glucose-to-LA conversions. Surface coverage of more than 30% by carbon residuals (as humins) was detected on both a-SA40 and a-SAPO25 at the end of the reaction, which can be partially removed by calcination at 450 °C (Table S2†).

To probe into the influence of the Brønsted and Lewis acid content on the overall glucose conversion to LA, we carried out further assessments on the range of a-SA series catalysts by using the fructose and 5-HMF intermediates as the starting reactants. Doing so allows specific probing of the subsequent reaction after glucose isomerization, i.e., fructose dehydration and 5-HMF rehydration. As shown in Fig. 8a, when fructose is used as the starting reactant, the optimum sample for LA yield was shifted to a-SA80 (36%), whereas the LA yield for a-SA40 decreased to 27%. In other words, the optimum LA yield shifted from the a-SA catalyst with a Brønsted acid-rich catalyst (B/L = 1.9) to one richer in Lewis acid (B/L = 0.70). This is unexpected since fructose formation from glucose isomerization has been claimed to rely on Lewis acid.¹⁰ Nevertheless, the result points to the greater influence of Lewis over Brønsted acid when starting with fructose, and vice versa for glucose. It should be reiterated that at any time the co-presence of both Lewis and Brønsted acid sites is a critical feature for attaining high LA yields. The almost exclusive Lewis acid of a-SA100 (i.e., pristine Al₂O₃) gave a low LA yield. Unlike the isomerization (of glucose to fructose) and dehydration (of fructose to 5-HMF) steps, the influence of different acidities of a-SA is less obvious in the rehydration step (of 5-HMF to LA) (Fig. 8b). Hence, it can be reasonably deduced that the final LA yield from the



Fig. 7 Glucose conversion and products yields over (a) a-SA and (b) a-SAPO solid acids at 180 °C. The a-SA40(HSA) and ZSM-5 (Al/(Si + Al) = 0.08) are represented as open and open cross symbols, respectively.



Fig. 8 (a) Fructose and (b) 5-HMF conversion and product yields over a-SA solid acids at 180 °C.



Fig. 9 Reusability of the a-SA40 solid acid catalyst for the conversion of glucose at 180 °C.

overall glucose conversion reaction is more greatly influenced by the acid properties of the a-SA especially in the early isomerization and dehydration steps. This is consistent with prior studies that identified these steps as having larger activation energies than the final rehydration step.^{8,9}

Lastly, Fig. 9 shows the good recyclability of the champion a-SA40 catalyst over 4 consecutive reaction runs. Complete conversion of glucose was obtained in all cases, with average 5-HMF, FA and LA yields of 10, 19 and 40%, respectively. Although calcination could partially remove the residue humins (see Table S2†), we adopted a less cumbersome approach of simply rinsing the catalysts with deionized water in between reaction cycles. This appears to be adequate in making sufficient active sites available for the subsequent reaction run.

4. Conclusions

We have successfully demonstrated the design of flame-made amorphous solid acids of silica-alumina (a-SA series) and silica-alumina-phosphate (a-SAPO series) for the conversion of glucose to LA. Despite being non-porous, it was possible to

obtain solid acids with SSA as high as 478 m² g⁻¹ with surface acid density comparable to that produced at a lower SSA. This shows the reproducibility of the catalyst surface during the direct scaling of the particle size by FSP. By systematically varying their compositions, it was possible to yield solid acids with tunable acidity, *i.e.*, the amount of strong and weak acids, as well as the ratio of Brønsted to Lewis acid sites (B/L). The solid acids were tested for the aqueous conversion of glucose as standalone catalysts, i.e., without the addition of liquid acids. Optimum LA yields of 40% or more were achieved for a-SA40 (among a-SA series) and a-SAPO25 (for a-SAPO series), outperforming the protonated ZSM-5 (17% yield) and zeolite X (21% yield) as well as those reported for the ion-exchange polymer resins under similar reaction conditions. While the mutual existence of Brønsted and Lewis acids is critical, the optimum glucose-to-LA yield is attributed to the highest B/L ratio of the flame-made solid acids. The influence of acidity of the catalysts is more prominent in the isomerization (of glucose to fructose) and dehydration (of fructose to 5-HMF) steps than the final rehydration (of 5-HMF to LA) step. The a-SA40 catalyst was shown to be highly recyclable, with just simple rinsing in between reaction cycles. This work showcases the potential of using the economical and scalable FSP-

derived solid acids for the wider biomass conversion applications, especially where regioselectivity as commonly associated with zeolite catalysts is not essential.

Conflicts of interest

There are no conflicts to declare.

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