

25 **Table S1.** EN values for metal cations and metal element. EN₁: EN values for metal cations with
26 the most common coordination numbers (CN). EN₂: EN values for metal element (zerovalent),
27 which is taken from Pauling's scale.

Cations	CN	EN ₁	Element	EN ₂
Li ⁺	4 ^a	1.043 ^b	Li	0.98 ^b
Na ⁺	6 ^a	1.024 ^b	Na	0.93 ^b
K ⁺	4 ^a	0.999 ^b	K	0.82 ^b
Rb ⁺	6 ^c	0.998 ^b	Rb	0.82 ^b
Cs ⁺	8 ^c	0.993 ^b	Cs	0.79 ^b

28 ^a Ref: M. Dudev, J. Wang, T. Dudev and C. Lim, *J. Phys. Chem. B*, 2006, **110**, 1889–1895.

29 ^b Ref: K. Li and D. Xue, *J. Phys. Chem. A*, 2006, 110, 11332–11337.

30 ^c Ref: D. Z. Caralampio, J. M. Martínez, R. R. Pappalardo and E. S. Marcos, *Phys. Chem. Chem.*
31 *Phys.*, 2017, 19, 28993–29004.

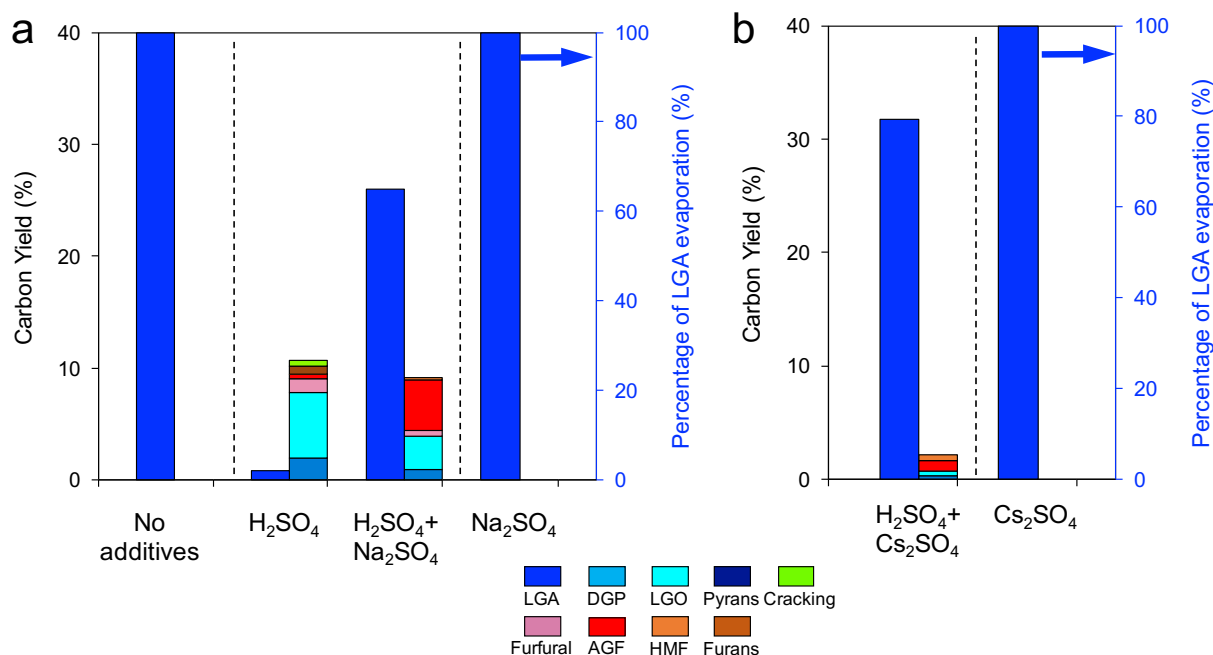
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34 **Salt-assisted LGA pyrolysis study**

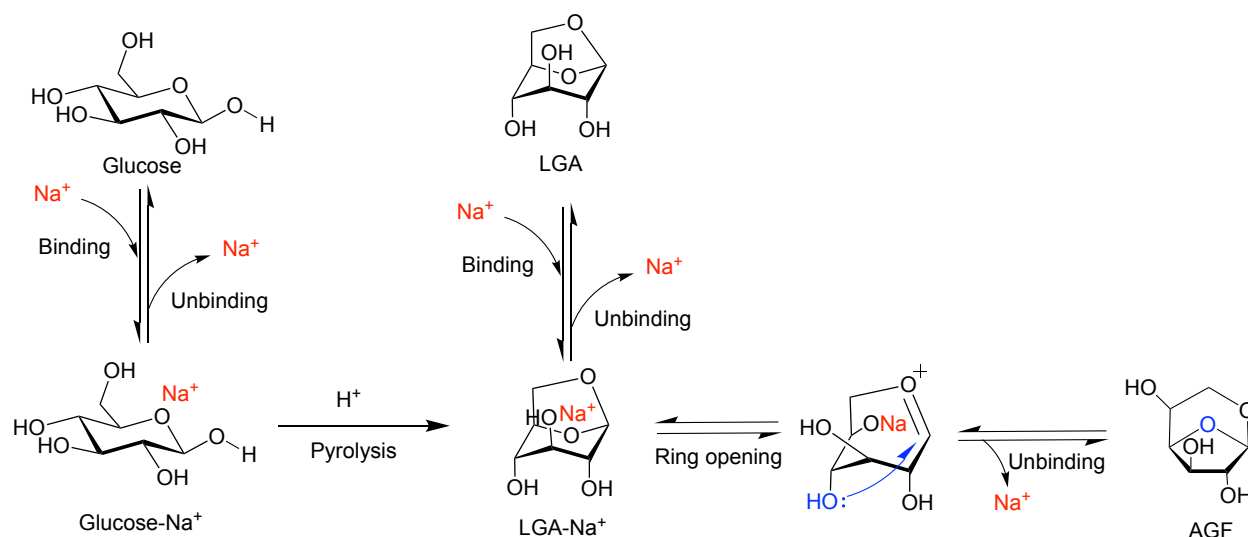
35 To test the hypothesis that AGF isomerizes from LGA, we treated LGA under our standard
36 pyrolysis conditions. LGA did not undergo any reaction by itself or co-mixed with Na₂SO₄ (Fig.
37 S2a). When combined with H₂SO₄ (2 mol%), >95% LGA was converted into LGO, DGP, and
38 furfural (with the rest of the carbon lost as char), indicating that LGA can undergo acid-catalyzed
39 reactions. Interestingly, when combined with Na₂SO₄ and H₂SO₄, less than 60% LGA reacted. The
40 total vapor-phase product yield decreased from ~11% to ~9%, with AGF yield increasing from
41 <1% to ~5%. These results indicate that the co-addition of Na₂SO₄ to the H₂SO₄-assisted pyrolysis
42 of LGA substantially inhibits its dehydration and ring-opening, and that AGF can indeed derive
43 from LGA.

44



45 **Fig. S2.** Pyrolysis of LGA with H₂SO₄ alone, or in combination with metal salt: (a) H₂SO₄/Na₂SO₄;
 46 (b) H₂SO₄/Cs₂SO₄. Conditions: levoglucosan mass = 28.8 μg (equimolar to glucose), H₂SO₄/LGA
 47 = 2 mol%, metal salt/LGA = 25 mol%, pyrolysis temperature = 350 °C, heating time = 60 s.
 48

49
 50 We suggest then that the AGF forms from acid-catalyzed pyrolysis of glucose by way of a Na⁺-
 51 associated LGA intermediate (Scheme S1).
 52



53 **Scheme S1.** Proposed reaction pathway involving Na⁺ association with glucose and *in situ*-
 54 generated LGA.
 55

56 We carried out the same LGA experiment but with $\text{Cs}_2\text{SO}_4/\text{H}_2\text{SO}_4$ in place of
57 $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$, to test idea that Cs^+ does not associate strongly enough with hydroxyl oxygens
58 and ether oxygen groups (Fig. 3c) to activate LGA for acid-catalyzed reaction. Indeed, more LGA
59 evaporated (from ~65% to ~80%) without conversion, and the total yield for all volatiles (e.g.,
60 DGP, LGO, AGF, HMF, etc.) was ~3% (lowered from ~9%) (Fig. S2b).