# Supplementary Information

## Bulk and composite catalysts combining BEA topology and mesoporosity for the valorisation of furfural

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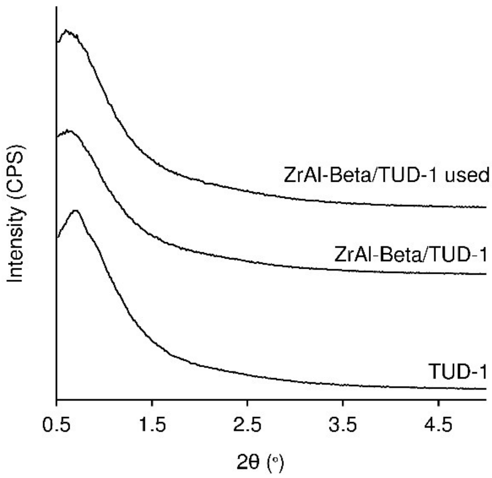


**Figure S1.** Low-angle X-ray diffractograms for mesoporous materials ZrAl-beta/TUD-1 (fresh and recovered after Fur conversion), and TUD-1.

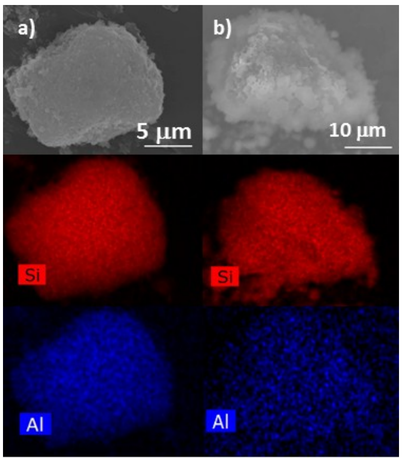


**Figure S2.** SEM and elemental (Si and Al) mappings of (a) H-beta-n and (b) deAl-beta-n.

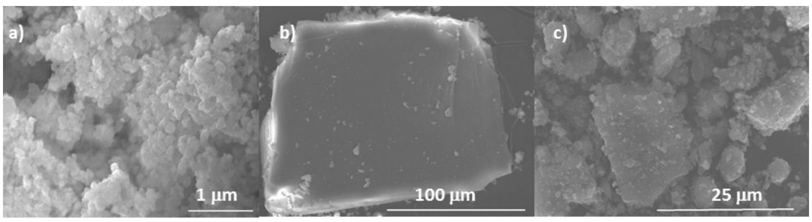


**Figure S3.** SEM of (a) ZrAl-Beta-n, (b) TUD-1 and (c) ZrAl-Beta/TUD-1.

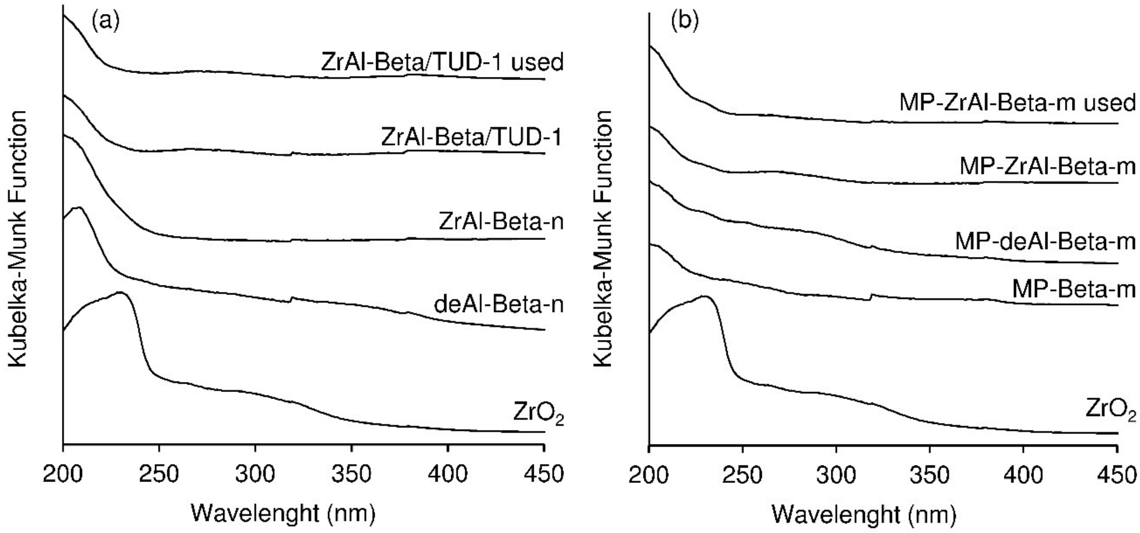


**Figure S4.** DR UV-vis spectra for (a) composite ZrAl-Beta/TUD-1 and related materials, and (b) MP-ZrAl-Beta-m and related materials.

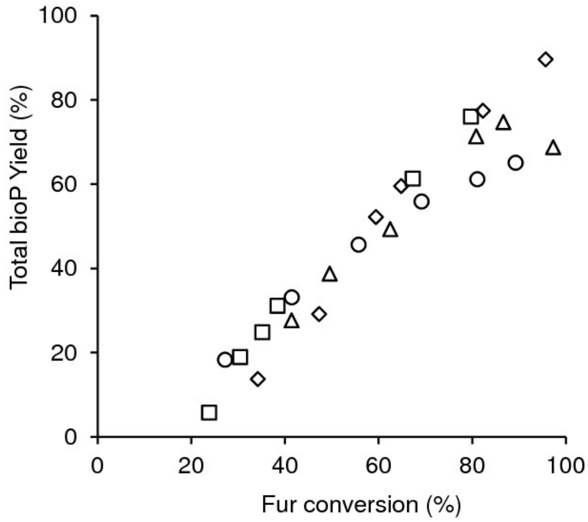


**Figure S5.** Influence of reaction temperature (T) and catalyst load (CatLoad) on total bioP yield as a function of Fur conversion, in the presence of ZrAl-beta/TUD-1, using 2-butanol as solvent and H-donor: (squares) (T=120 °C, CatLoad=12.9 $g_{cat}$ $dm^{-3}$); (circles) (T=120 °C, CatLoad=25.7 $g_{cat}$ $dm^{-3}$); (diamonds) (T=150 °C, CatLoad=12.9 $g_{cat}$ $dm^{-3}$); (triangles) (T=150 °C, CatLoad=25.7 $g_{cat}$ $dm^{-3}$).

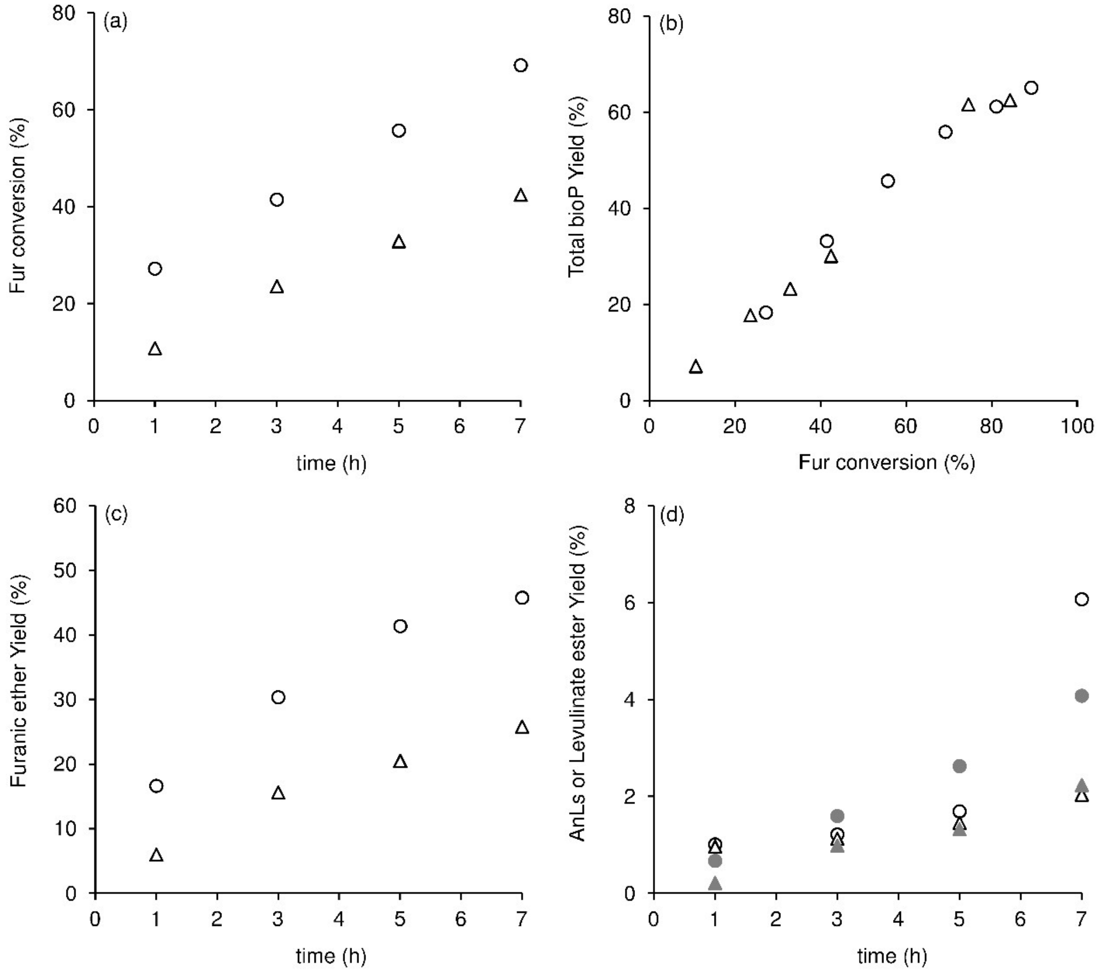


**Figure S6.** Influence of using 2-butanol (circles) or 2-propanol (triangles) as reacting solvent on (a) Fur conversion, (b) total bioP yield dependence on conversion, (c) furanic ether yield dependence on time, (d) AnLs (unfilled symbols) and levulinate ester (grey symbols) yield dependencies on time, in the presence of ZrAl-beta/TUD-1. The furanic ether and levulinate ester were 2BFE (circles) and 2BL (circles), respectively, for 2-butanol as solvent, and 2PFE (triangles) and 2PL (triangles), respectively, for 2-propanol as solvent. Reaction conditions: 0.45 M Fur, CatLoad=25.7 $g_{cat}$ $dm^{-3}$, T=120 °C.

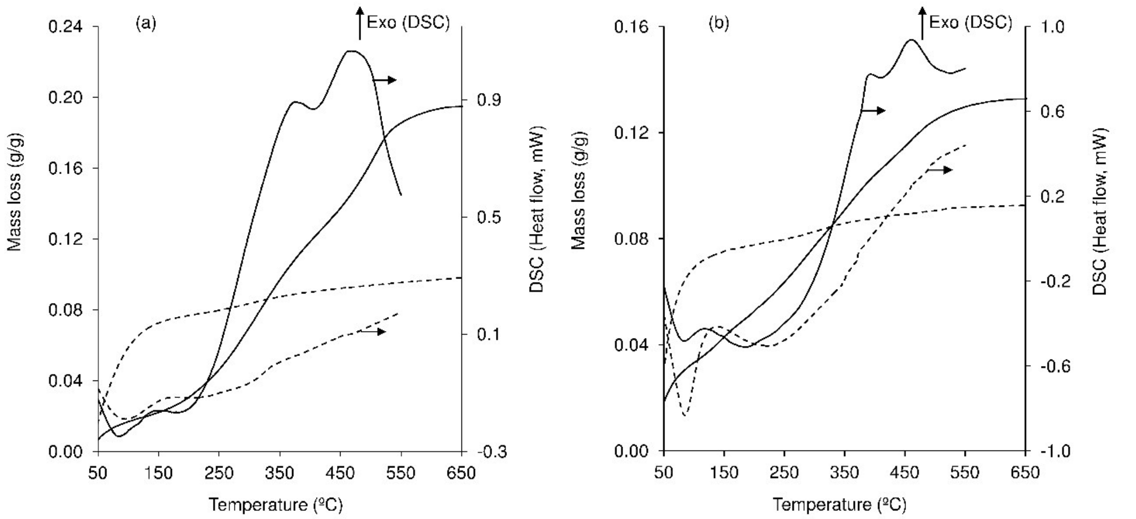


**Figure S7.** DSC and TGA analyses of fresh (dashed lines) and used catalysts (solid lines): (a) ZrAl-Beta/TUD-1 and (b) MP-ZrAl-Beta-m. The catalysts were used for Fur/2BuOH reaction (0.45 M Fur, CatLoad=25.7 $g_{cat}$ dm$^{-3}$, T=150 °C).

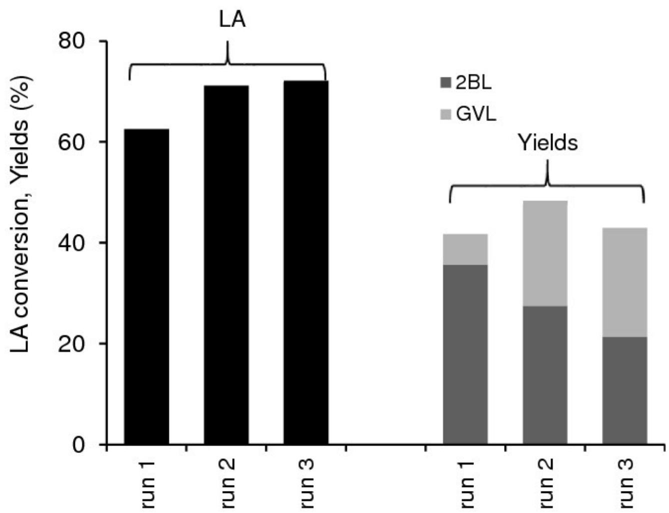


**Figure S8.** LA conversion and bioP yields for consecutive batch runs using the composite catalyst ZrAl-Beta/TUD-1. Reaction conditions: 0.45 M Fur in 2BuOH, T=150 °C, 24 h, CatLoad=25.7 $g_{cat}$ dm$^{-3}$.

**Table S1.** Reaction of Fur at 120 ºC, in the presence of ZrAl-Beta/TUD-1, H-Beta (similar sample to H-Beta-n) or mixtures of H-Beta-n and Zr-containing materials.[a]

| Catalyst | Conv. (%)[b] | bioP yields at 24 h (%) | | | Total bioP yield[b] (%) | LA yield (%) |
|---|---|---|---|---|---|---|
| | | 2BFE | 2BL | AnLs | | |
| ZrAl-beta/TUD-1 | 81 | 45 | 9 | 7 | 61 | <1 |
| H-beta-n + ZrAl-beta/TUD-1 [b] | 57 | <1 | 5 | 7 | 12 | 3 |
| H-beta-n + ZrAl-beta-n [b] | 73 | <1 | 9 | 11 | 20 | 9 |
| H-beta [c] | 43 | - | 3 | 4 | 7 | 2 |

[a] Reaction conditions: 0.45 M $[Fur]_0$ in 2-butanol, total CatLoad=25.7 $g_{cat}$ $dm^{-3}$, T=120 °C, 24 h. [b] Mechanically mixed materials used in mass ratio of 1.[c] Results for H-beta were taken from ref.[2], and this sample was prepared in a similar fashion to H-beta-n. GVL yield was always less than 2%.

**Table S2.** Reaction of Fur in the presence of the synthetic precursors of MP-ZrAl-beta-m.[a]

| Catalyst | Conv. (%)[b] | bioP yields at 24 h (%) | | | Total bioP yield[b] (%) |
|---|---|---|---|---|---|
| | | 2BFE | 2BL | AnLs | |
| H-beta-m | 24 | 0 | 3 | 2 | 5 |
| OxAc-beta-m | 38 | 0 | 5 | 1 | 6 |
| MP-beta-m | 12 | 0 | 0 | <1 | <1 |
| deAl-MP-beta-m | 16 | 5 | 1 | 1 | 7 |

[a] Reaction conditions: 0.45 M $[Fur]_0$ in 2-butanol, total CatLoad=25.7 $g_{cat}$ $dm^{-3}$, T=150 °C, 24 h.

## References

1. M. M. Antunes, S. Lima, P. Neves, A. L. Magalhães, E. Fazio, F. Neri, M. T. Pereira, A. F. Silva, C. M. Silva, S. M. Rocha, M. Pillinger, A. Urakawa and A. A. Valente, *Applied Catalysis B: Environmental*, 2016, **182**, 485-503.
2. M. M. Antunes, S. Lima, P. Neves, A. L. Magalhães, E. Fazio, A. Fernandes, F. Neri, C. M. Silva, S. M. Rocha, M. F. Ribeiro, M. Pillinger, A. Urakawa and A. A. Valente, *Journal of Catalysis*, 2015, **329**, 522-537.