

Extended Supplementary Information for:

Bifunctional Lewis and Brønsted acidic zeolites permit the continuous production of bio-renewable furanic ethers

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Table S1. Metal content and porosity data for various aluminosilicate and stannosilicate materials. Al content determined by ICP-MS, Sn content determined by EDX spectroscopy and porosity data determined by N₂ isotherms; Brunauer-Emmett-Teller surface area (S_{BET}) calculated from BET method, and micropore volume (V_{micro}) derived from the t-plot method

| Entry | Catalyst | Al wt. % | Sn wt. % | aS_{BET} ($\text{m}^2 \text{g}^{-1}$) | V_{micro} ($\text{cm}^3 \text{g}^{-1}$) |
|-------|--------------|----------|----------|--|--|
| 1 | H-Beta-38 | 2.30 | - | 551 | 0.210 |
| 2 | deAl-Beta-38 | < 0.05 | - | 596 | 0.221 |
| 3 | 2Sn-Beta | < 0.05 | 1.7 | 563 | 0.191 |
| 4 | 10Sn-Beta | < 0.05 | 9.4 | 525 | 0.193 |

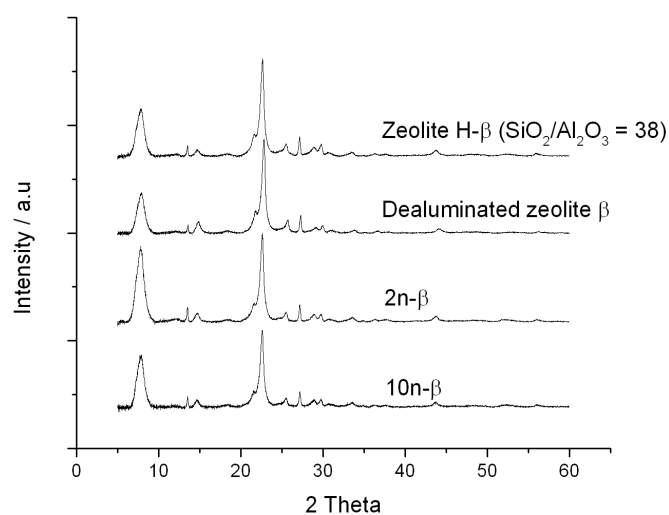


Figure S1. XRD analysis of different aluminosilicate and stannosilicate catalysts, including (from top to bottom) zeolite H-Beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 38$), dealuminated zeolite beta, 2Sn-Beta and 10Sn-Beta.

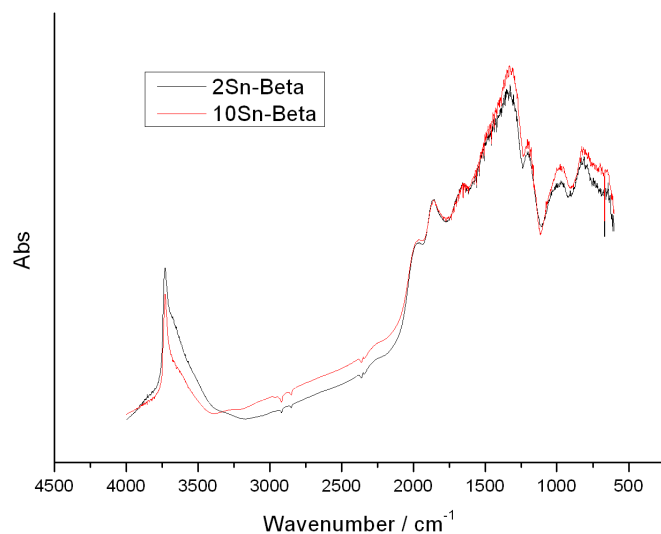


Figure S2. FTIR analysis of 2Sn- β and 10Sn- β following outgassing at 550 °C. The intensities are normalised to the Si-O-Si absorbances, so that the relative intensities of the OH region bands can be compared.

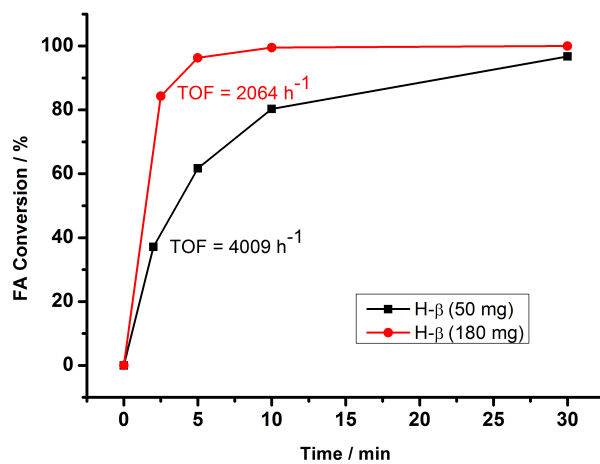


Figure S3. Conversion of FA to BMF as a function of time using H-Beta (300) at different mass loading. Initial TOF is displayed for the two different loadings.

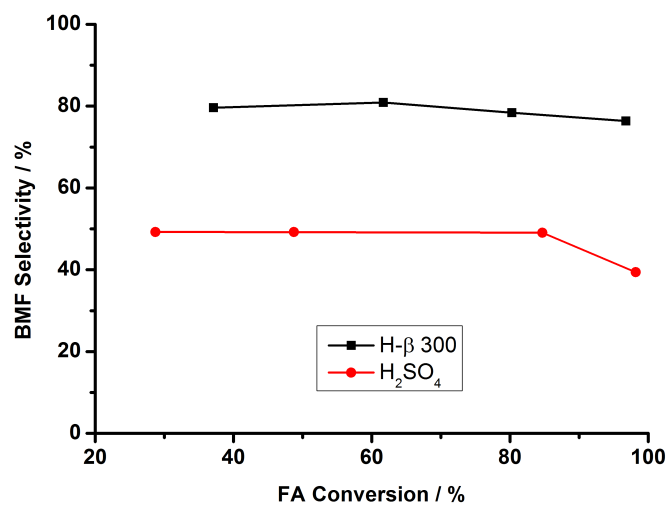


Figure S4. BMF selectivity as a function of FA conversion for H-Beta 300 and sulfuric acid.

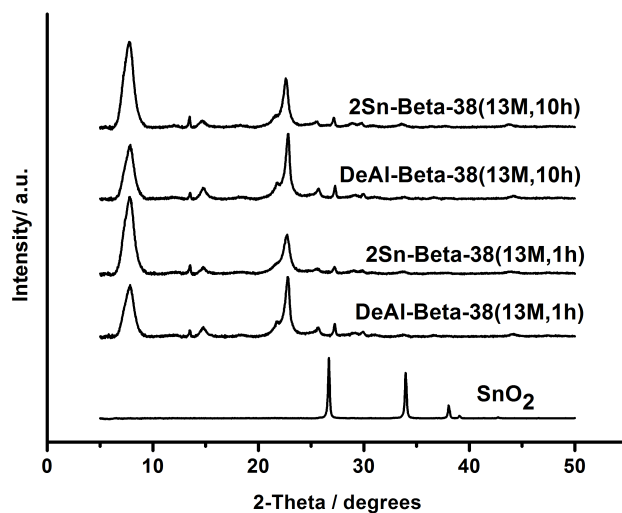


Figure S5. XRD patterns of zeolites treated at different conditions. The dealumination time and concentration are in parentheses. From top to bottom: 2Sn-Beta-38 (13M, 10h), DeAl-Beta-38 (13M, 10h), 2Sn-Beta-38 (13M, 1h), DeAl-Beta-38 (13M, 1h) and SnO₂.

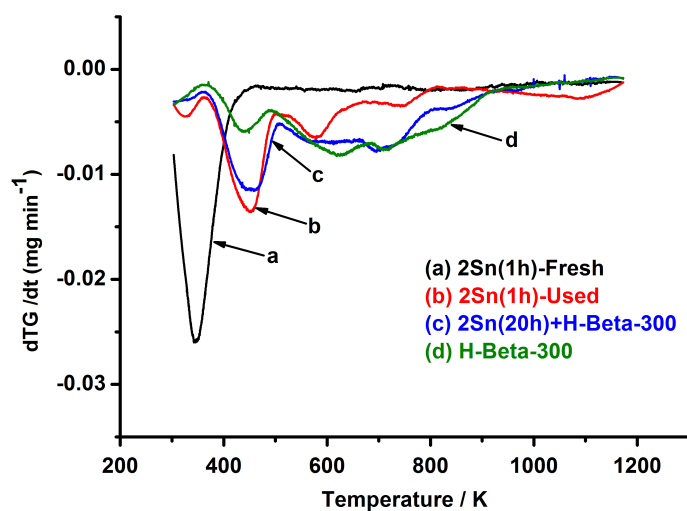


Figure S6. Thermogravimetry analysis of different used catalysts compared against a fresh sample: a) 2Sn(1h) fresh, b) 2Sn(1h) used after FF MPV/etherification, c) physical mixture used after FF MPV/etherification and d) H-Beta 300 used after FA etherification only.

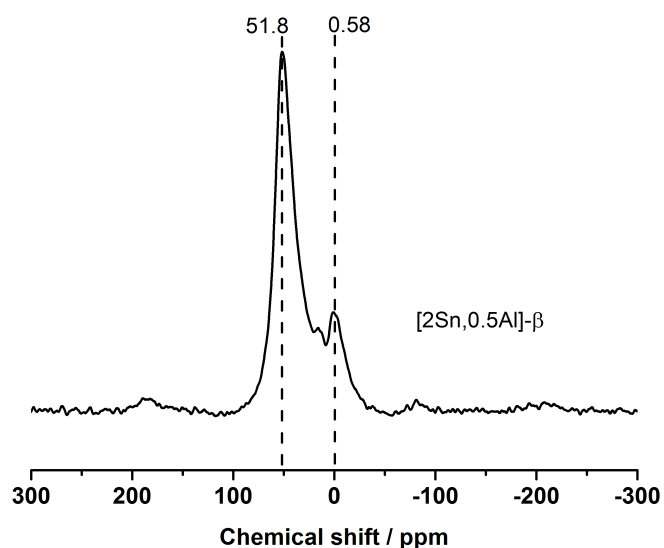


Figure S7. ^{27}Al MAS NMR spectrum of [2Sn, 0.5Al]- β .

Table S2. Porosity data of various fresh, used and regenerated alumino- and stanno-silicate catalysts. Brunauer-Emmett-Teller surface area (S_{BET}) calculated from BET method, and micropore volume (V_{micro}) derived from the t-plot method. Values in italic and underlined correspond to measurements made on used (*i.e. ex reactor*) and regenerated catalyst mixtures, respectively.

| Catalyst | $^a S_{\text{BET}}$ ($\text{m}^2 \text{g}^{-1}$) | V_{micro} ($\text{cm}^3 \text{g}^{-1}$) |
|--|--|--|
| Al-BEA-38 | 550.38 | 0.247 |
| [2Sn,0.5Al]- β undiluted | 560.716 | 0.245 |
| [2Sn,0.5Al]- β (1:4 by weight physical mixture with SiC) | 53.432 (after reaction) <u>93.482</u> (after reaction + regeneration) | 0.022 (after reaction) <u>0.043</u> (after reaction + regeneration) |

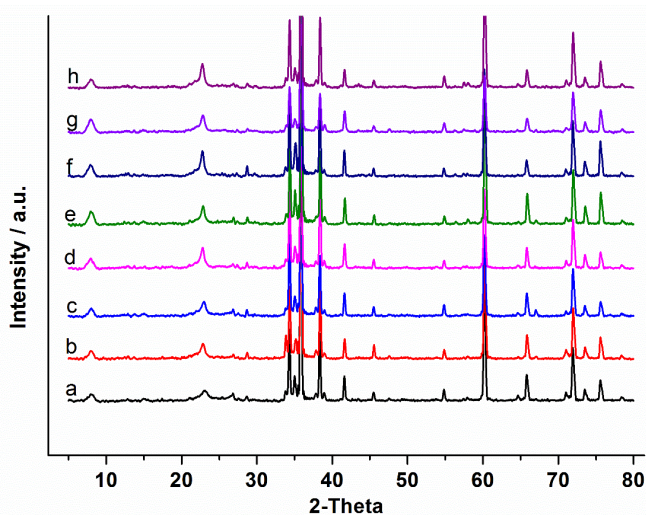


Figure S8. XRD of different fresh and used zeolite catalysts (20 wt. %) mixed with SiC (80 wt%). From bottom to top: a) 2Sn(1h)-Beta fresh, b) 2Sn(1h)-Beta used, c) 2Sn(10h)-Beta fresh, d) 2Sn(10h)-Beta used, e) 2Sn(20h)+H-Beta fresh, f) 2Sn(20h)+H-Beta used, g) 2Sn-0.5Al-Beta fresh and h) 2Sn-0.5Al-Beta used.