Renewable short-chain olefin production through dehydration reactions over nano-HZSM-5/γ-Al_2O_3 hybrid catalysts

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Supporting information

(S1) Schematic route to synthesize the hybrid catalyst

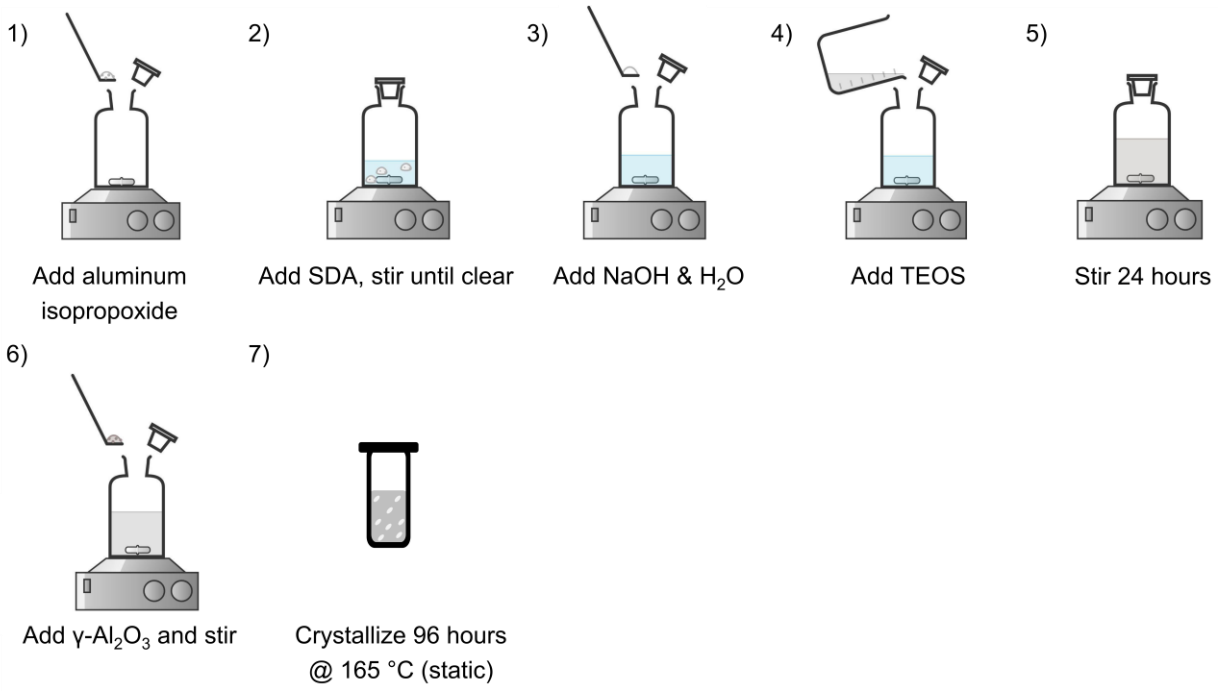

Figure S1: Schematic representation of hybrid catalyst synthesis (SDA = structure directing agent, in our case tetrapropyl ammonium hydroxide, TEOS = tetraethyl orthosilicate). The lab equipment is drawn with Chemix (https://chemix.org)

Some extra remarks regarding the synthesis route:

1) Important to note is that dissolving the aluminum isopropoxide in the TPAOH is quite slow, therefore we typically stir this mixture for about 2 hours, before adding any NaOH or H_2O.
2) When adding H_2O, one should account for the water which is already in the SDA (which is dependent on the purity of the SDA solution).
3) In literature the addition of TEOS (for the synthesis of ZSM-5) is typically done dropwise
4) The amount of γ-Al_2O_3 that has to be added is dependent on the amount of ZSM-5 that will be formed during the crystallization. To estimate the amount of ZSM-5 that would be obtained, (1) we calculated the molar mass of ZSM-5 based on the general formula of ZSM-5 ($Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$) and the desired Si/Al ratio. Based on the molar mass we (2) predicted the amount of ZSM-5 that could be formed. (3) By synthesizing multiple batches of nano-ZSM-5, we could estimate what the typical yield is and we used this value as an estimate for the ZSM-5 yield to add the same mass of γ-Al_2O_3.

(S2) NH_3-TPD

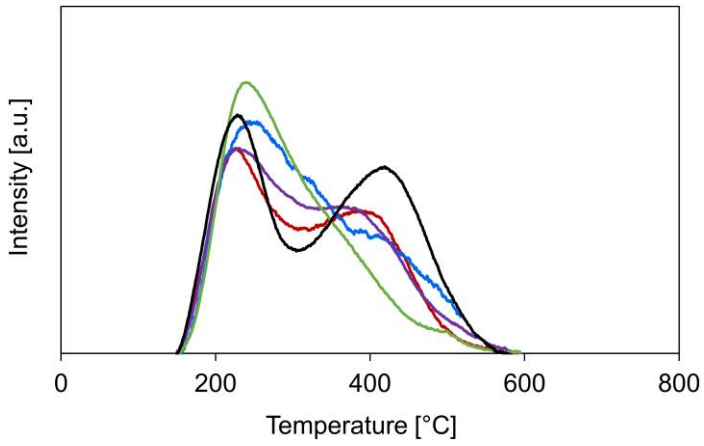

Figure S2. NH_3-TPD spectra for c-HZSM-5 (black), n-HZSM-5 (red), PM-50/50 (grey), Hybrid-50/50 (green) and γ-Al_2O_3 (blue). Starting temperature = 150 °C, heating ramp = 10 K min^{-1}, the intensities are weight-normalized.

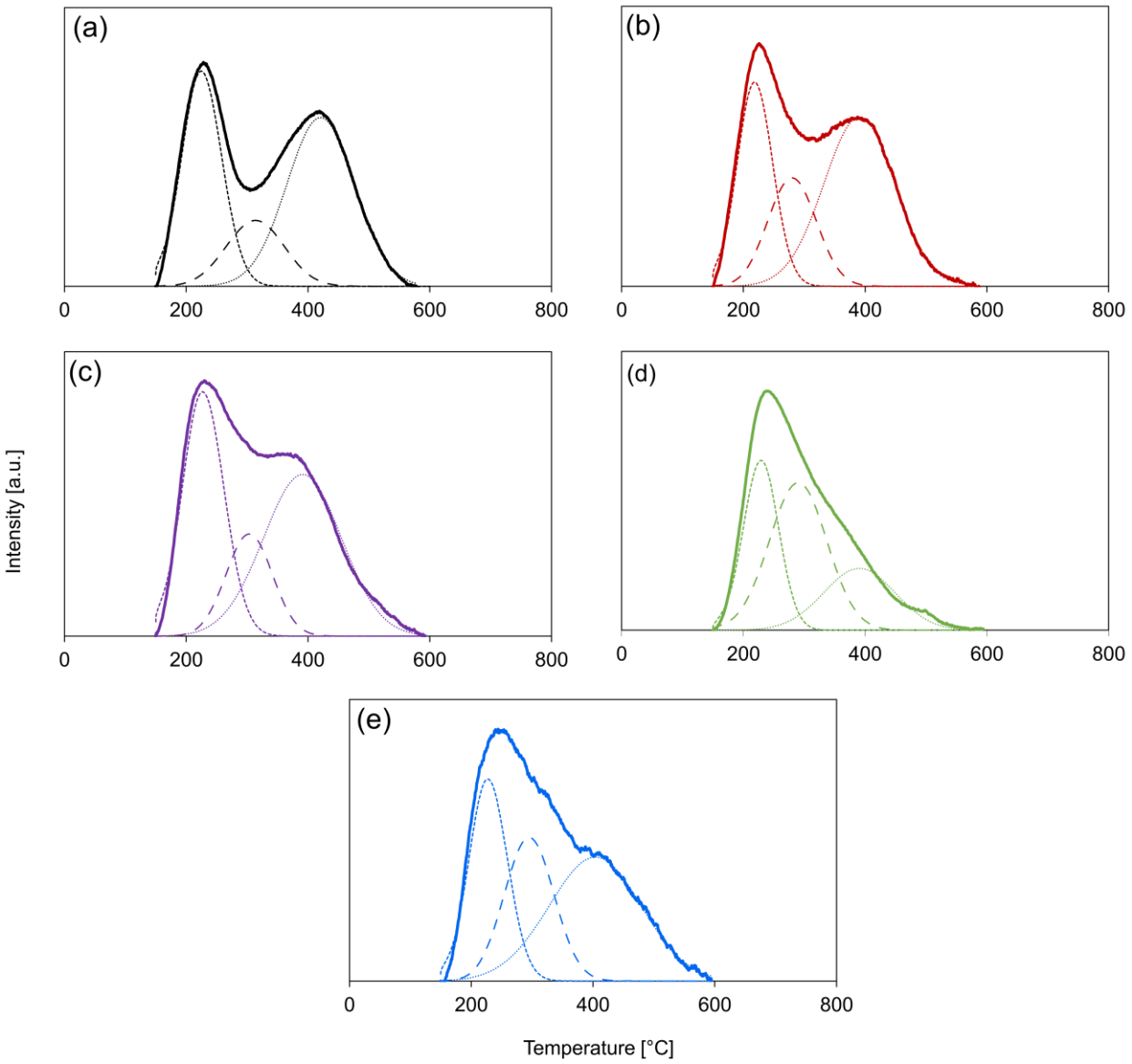

Figure S3. NH_3-TPD profiles with deconvolution of c-HZSM-5 (a), n-HZSM-5 (b), PM-50/50 (c), Hybrid-50/50 (d) and γ-Al_2O_3 (e). The weak acid site contribution to the spectrum is depicted as (---), the medium acid sites as (-·-) and the strong acid sites as (···).

(S3) SEM-images

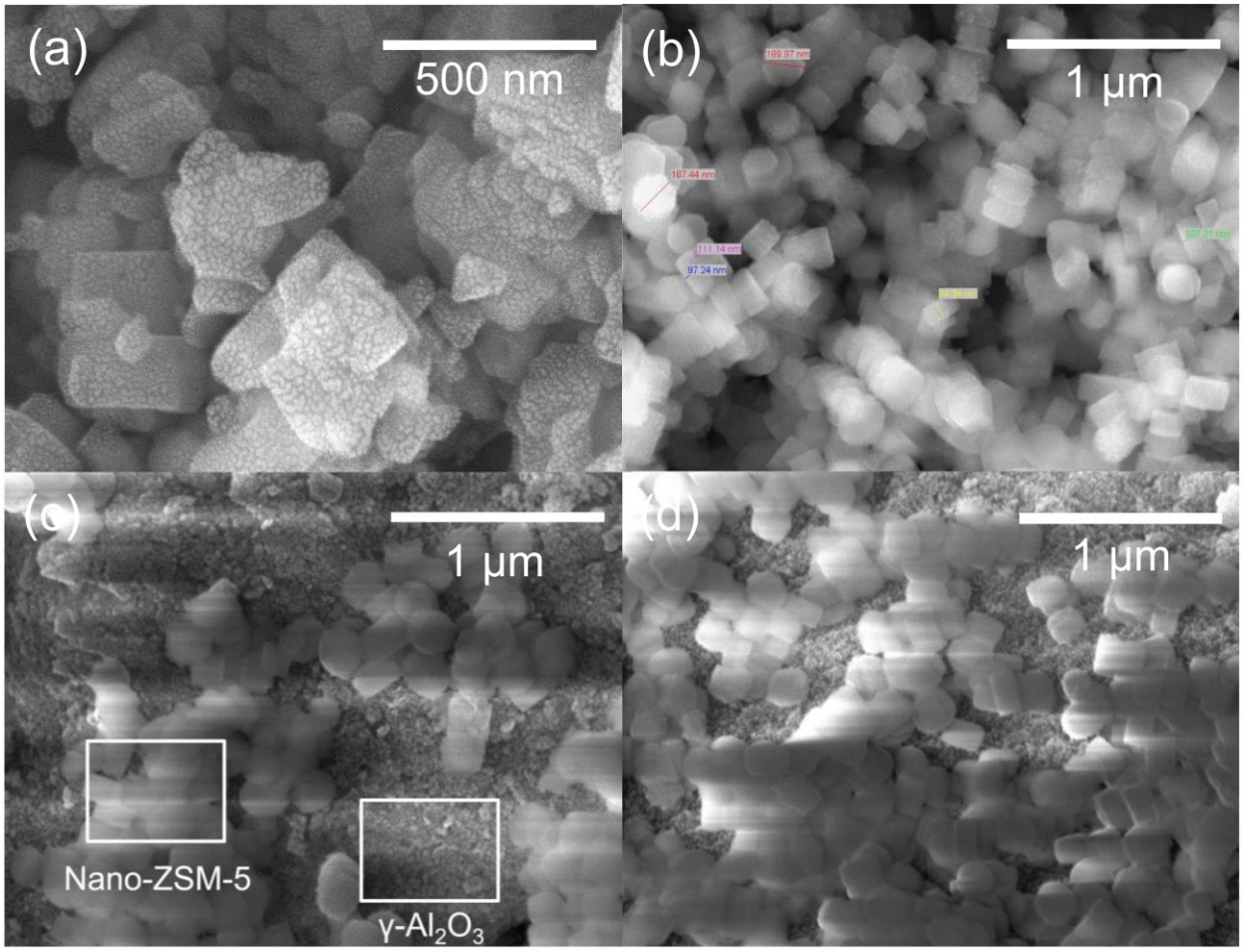

Figure S4. SEM-images of c-HZSM-5 (a) n-HZSM-5, with crystal size bars (b) and Hybrid-50/50 (c,d).

The irregularities on the crystals of c-HZSM-5 are the gold nanolayers on top of the crystals to increase resolution of the SEM. In (d) the coffin-shape of the in-situ synthesized nano-HZSM-5 crystals is clearly visible.

(S4) Selectivity comparison

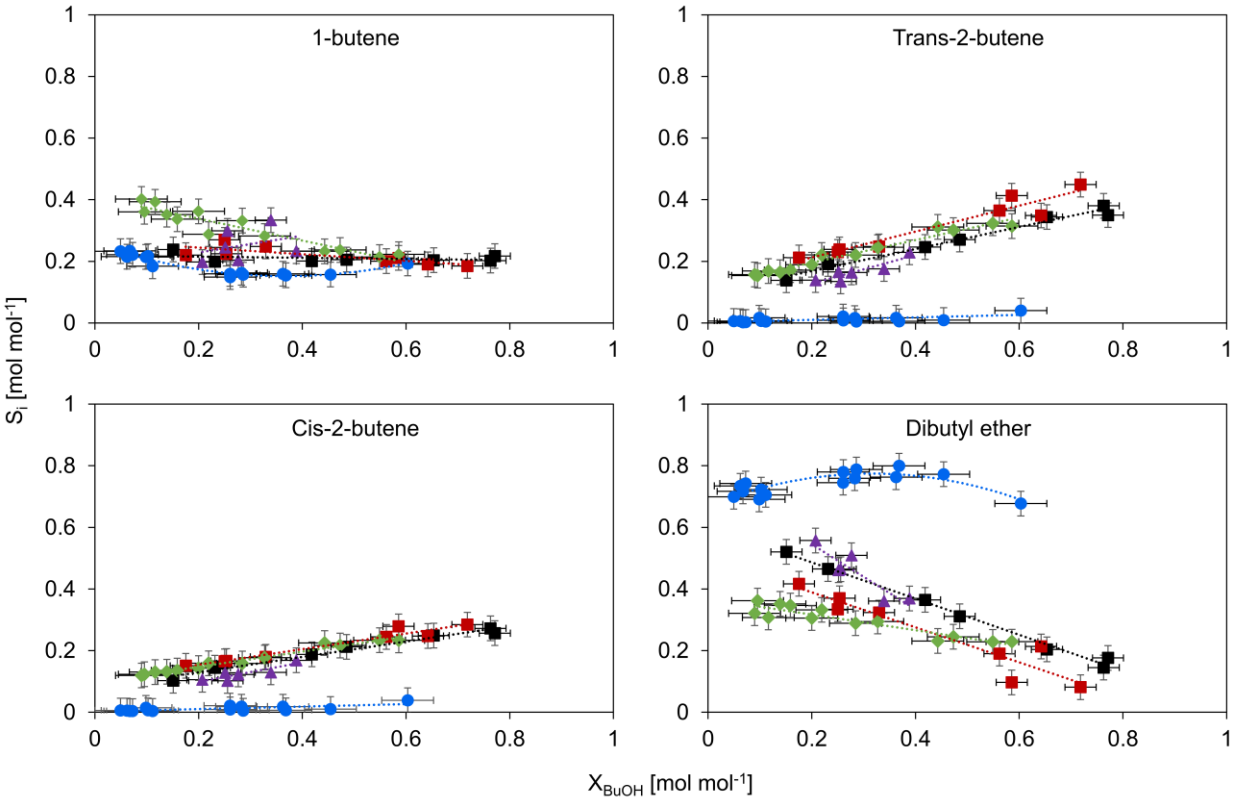

Figure S5. Selectivity of products versus conversion, c-HZSM-5 (■, black), n-HZSM-5 (■, red), PM-50/50 (▲, purple), Hybrid-50/50 (◆, green) and γ-Al2O3 (●, blue). Temperature = 513 K, inlet pressure of n-butanol = 29 kPa, total pressure = 5 bar. Error bars indicate the 95% confidence interval.

The selectivities displayed in Figure S5 are the same as in Figure 6, but now error bars are added. In Figure 6, these error bars are left out to increase readability.