Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Highly stable amorphous silica-alumina catalysts for continuous bio-derived mesitylene production under solvent-free conditions

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Catalytic studies in batch experiments

For catalytic reactions under batch conditions, typically 10 g acetone and 5 wt% catalyst were added to the autoclave (45 mL, Parr) which was then pressurized with 40 bar Ar and heated to 230 °C while stirring at 500 rpm. After completion of the reaction, filtered samples of the reaction mixture were analyzed using gas chromatography (Shimadzu GC-2010 Plus with FID, Restek RTX-5 Amine, 40-250 °C, 10 K min^{-1}, He) and 1,4-dioxane (99.5 %) as an internal standard. Furthermore, the identification of products was confirmed by GC coupled with mass spectrometry (Shimadzu GCMS-QP2010SE).

Calculation of conversion *X*, product yield *Y*, and selectivity *S*:

Conversion of alkyl methyl ketone *X*:

$$X_{\mathrm{Ketone}} = 1 - \frac{n_{\mathrm{Ketone}}}{n_{\mathrm{Ketone,0}}}$$

with *n*: substance amount in mol

Product yield *Y*:

$$Y_i = \frac{|\nu_{\mathrm{Ketone}}| n_i}{\nu_i \, n_{\mathrm{Ketone,0}}}$$

with ν: stochiometry of the reactant in the reaction

Product selectivity *S*:

$$S_i = \frac{Y_i}{X_{\mathrm{Ketone}}}$$

The substance amounts are obtained via response factors *RF* based on the internal standard (IS) 1,4-dioxane obtained from GC-calibration, and the measured substance areas *A*. In case of acetone as starting ketone, calibration substances were used for mesityl oxide (dimer), mesitylene (aromatic), and isophorone (trimer).

$$\frac{A_i}{A_{\mathrm{IS}}} = \frac{w_i}{w_{\mathrm{IS}}} RF$$

with *w*: weight fraction

For the higher alkyl methyl ketone 2-butanone, only the ketone and the aromatic triethylbenzene were available for calibration. Therefore, the concept of the effective carbon number (*ECN*) with the relative response factors *RRF* was used based on the molecular weight (*MW*) and calculated *ECN* of the substance and a structurally similar reference substance *R*.[1-2]

$$RRF_i = \frac{MW_i}{MW_R} \cdot \frac{ECN_R}{ECN_i}$$

The reference substances are the corresponding dimers and trimers of the acetone condensation. The many positional isomers existing for the products of 2-butanone were grouped together and the corresponding area sums were used for calculation.

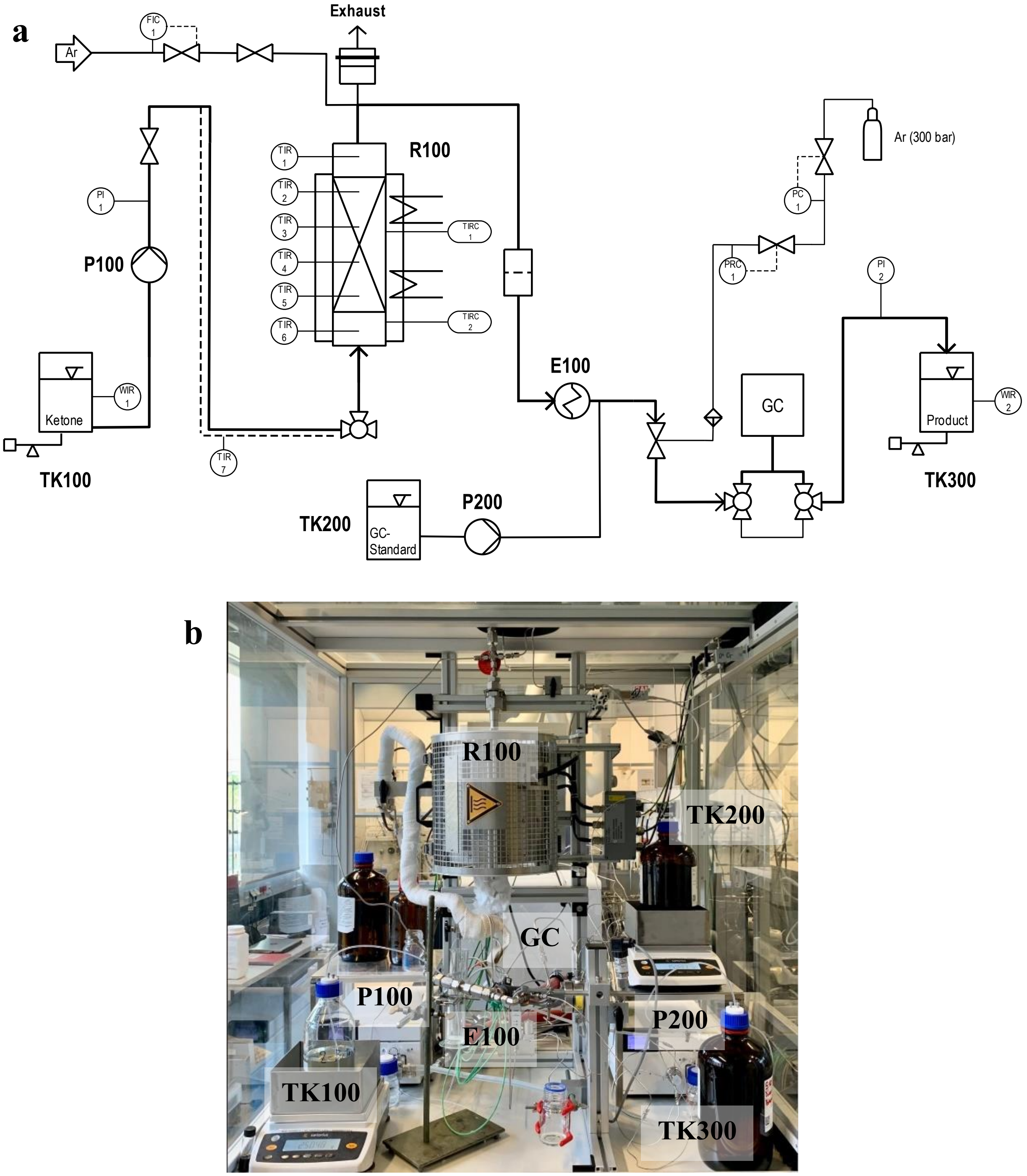

Figure S1: Process flow diagram of the catalytic fixed-bed reactor (a) and frontal view of the reactor (b).

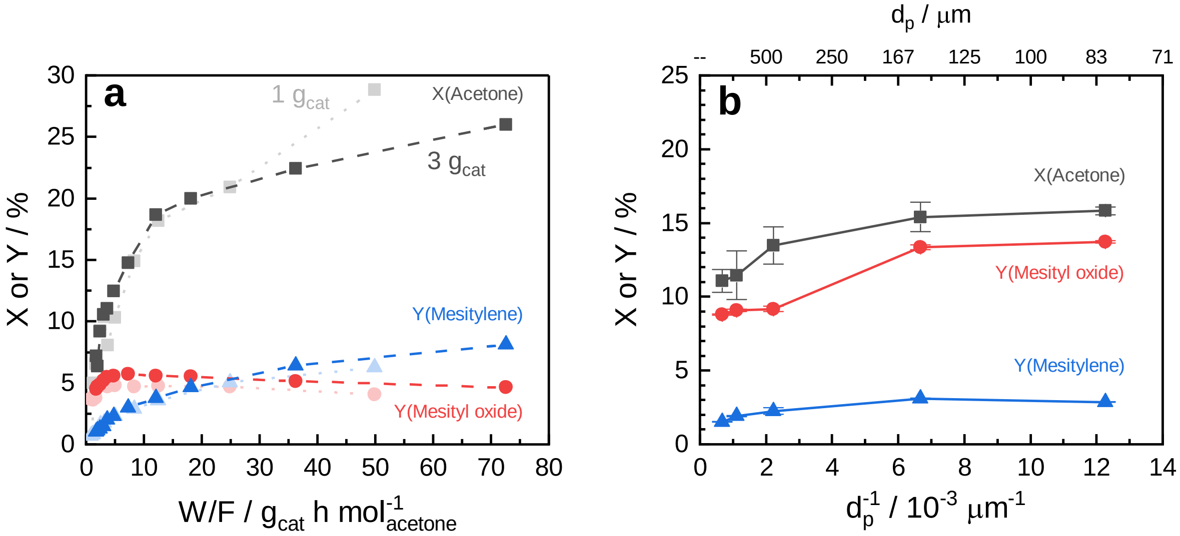

Figure S2: Assessment of external (a) and internal (b) mass transfer limitations at 210 °C.

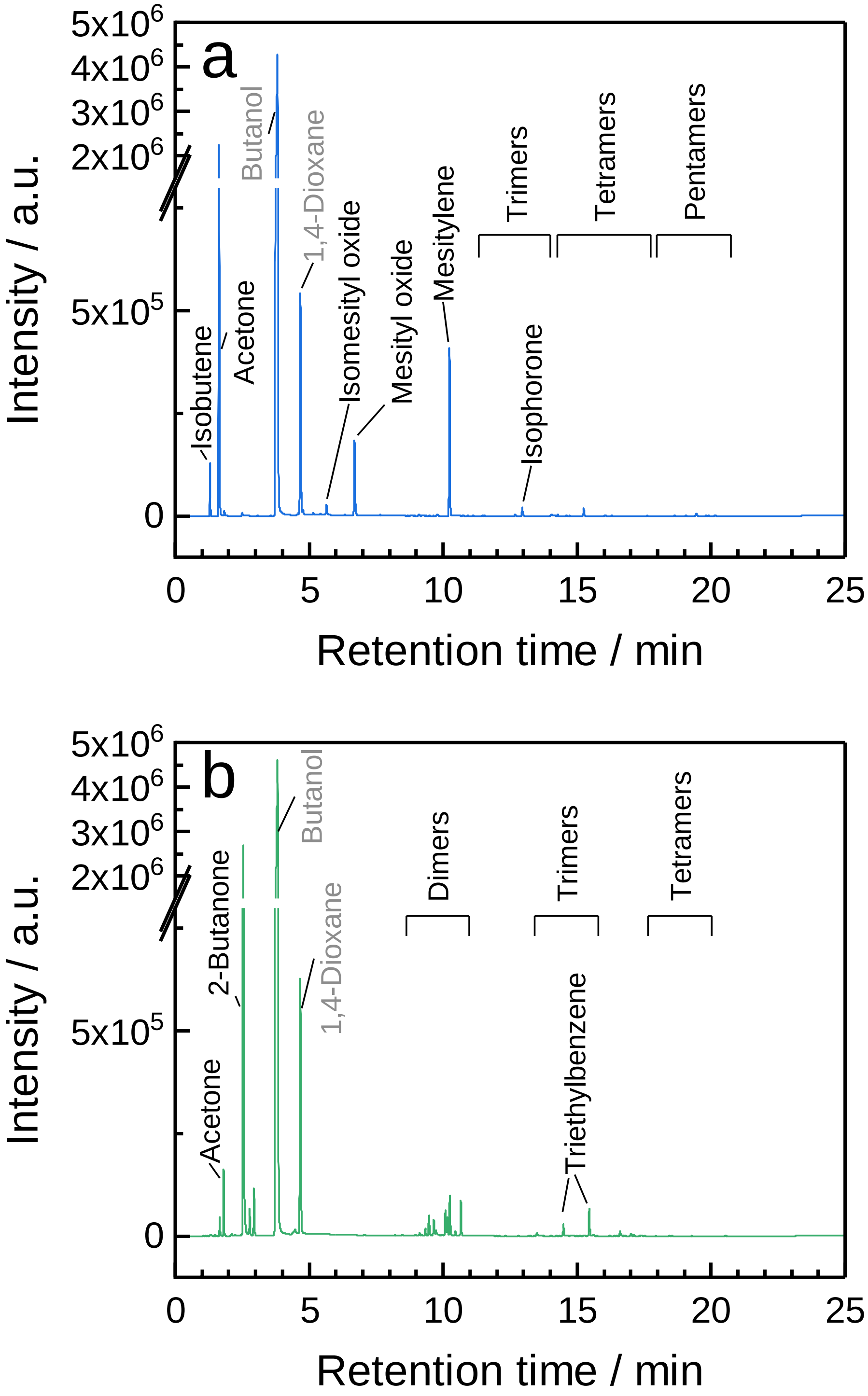

Figure S3: Representative GC-chromatograms of the product mixture for the conversion of acetone (a) and 2-butanone (b) at 260 °C in the fixed-bed reactor using Siralox 30. 1,4-Dioxane is used as internal standard and 1-butanol for dilution.

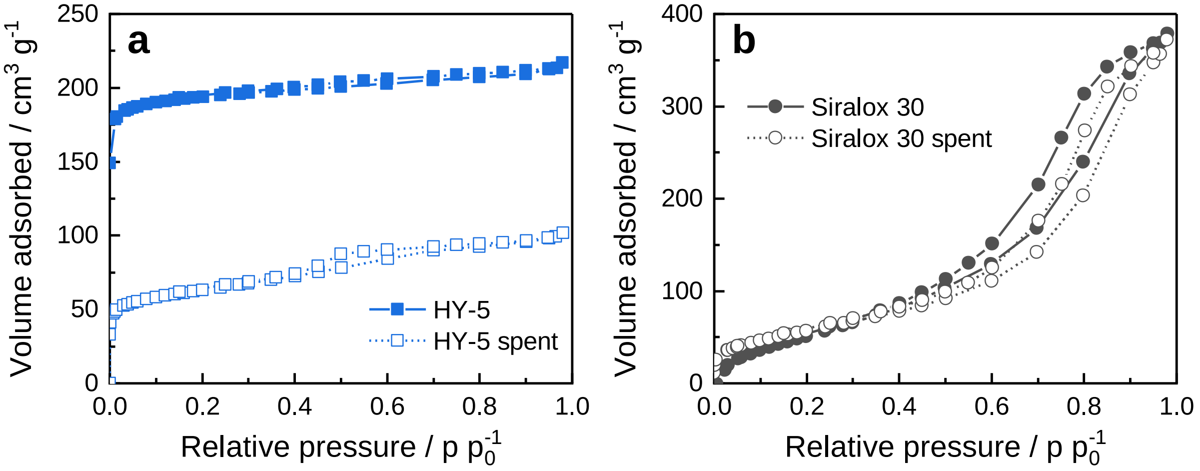

Figure S4: N_2-Physisorption data for fresh and spent HY-5 (a) and Siralox 30 (b).

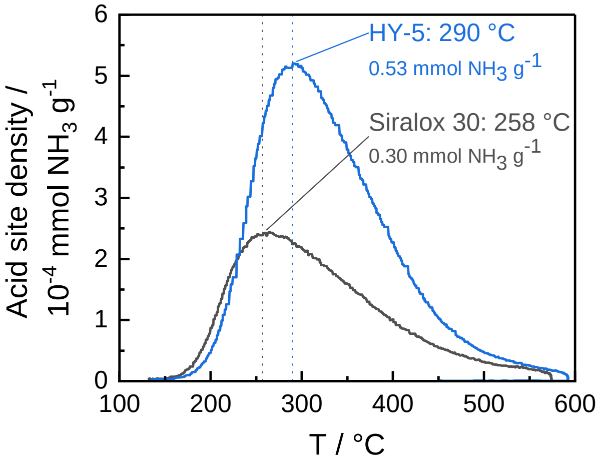

Figure S5: NH_3-TPD curves for Siralox 30 and HY-5 catalyst and maxima of their desorption temperature.

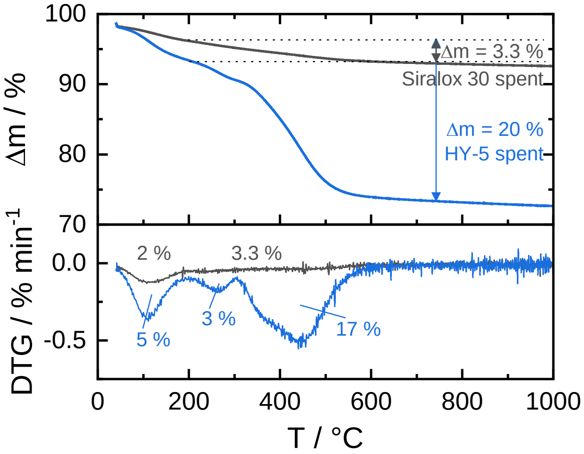

Figure S6: TGA and DTG curves for spent HY-5 and Siralox 30 catalyst in air. After the reaction HY-5 showed clear signs of black carbonaceous deposits while Siralox 30 remained grey-white. The chemical nature of the depositions was classified as following: < 180 °C: water and volatile species, 180-330 °C: “soft coke”, 330-750 °C: bulky carbonaceous deposits (“hard coke”) according to Sahoo et al.[3]

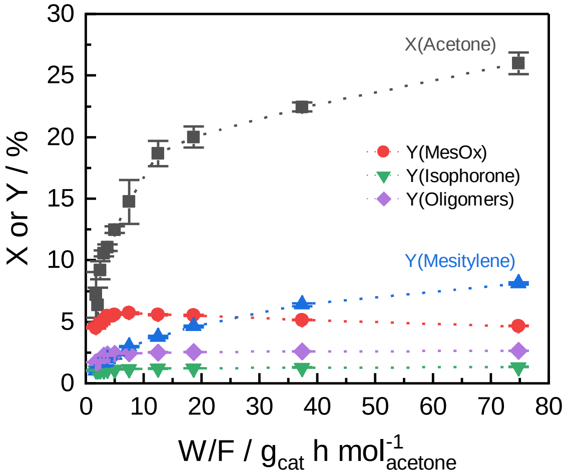

Figure S7: Acetone conversion and product yields for Siralox 30 at 210 °C for varying catalyst contact times.

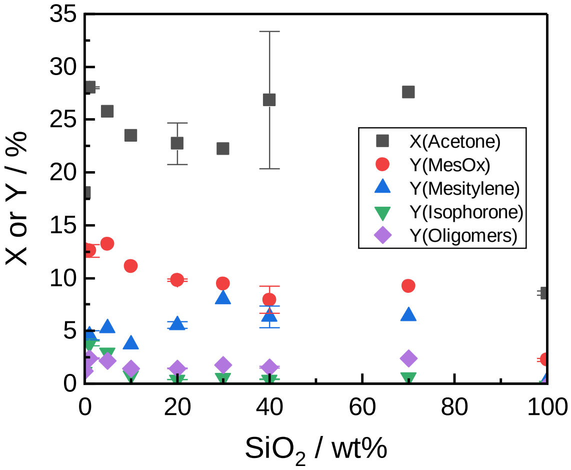

Figure S8: Acetone conversion and product yields of batch reactions at 230 °C (3 h) for varying silica content.

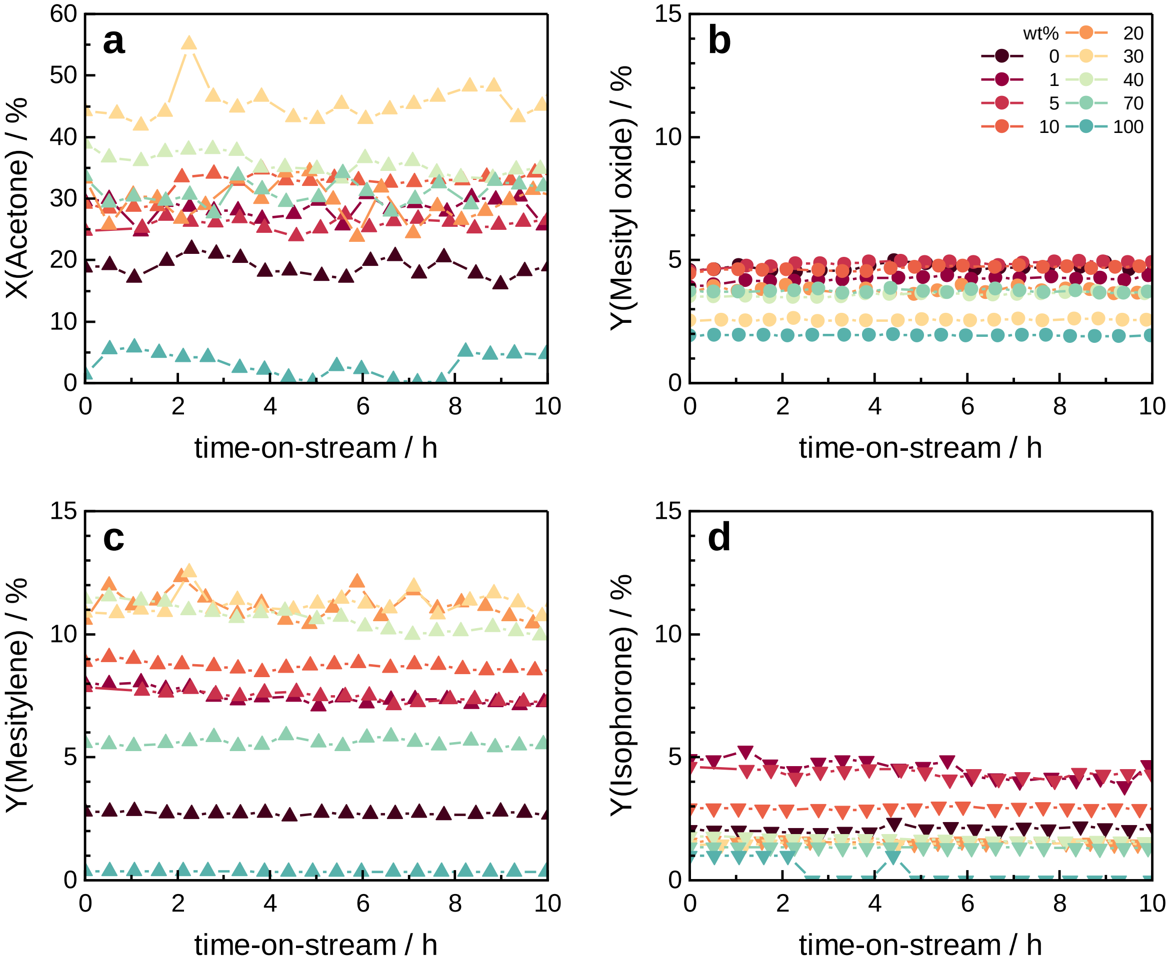

Figure S9: Silica-alumina catalyst stability based on acetone conversion (a) and product yields of mesityl oxide (b), mesitylene (c), and isophorone (d) for varying silica content (in wt%) in the flow reactor at 260 °C, 12.5 g_{cat} h mol^{-1}.

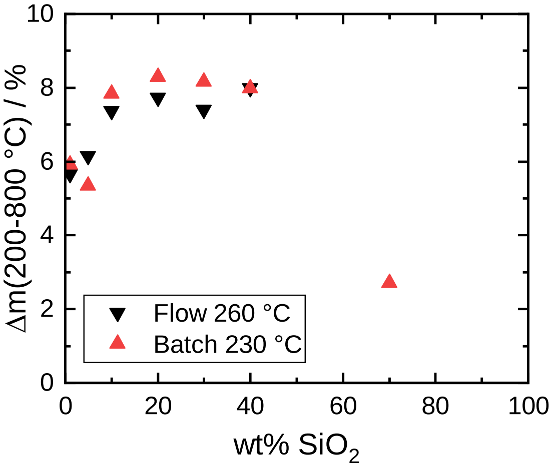

Figure S10: Mass loss of the spent catalysts determined by TGA (5 K min^{-1}, 40-1000 °C) in air.

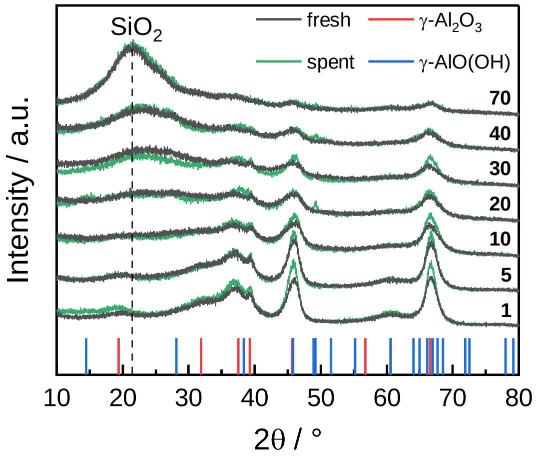

Figure S11: XRD spectra of fresh and spent (flow reactor, 260 °C, 12.5 g_{cat} h mol^{-1}) Siralox catalysts of varying silica-content in wt%.

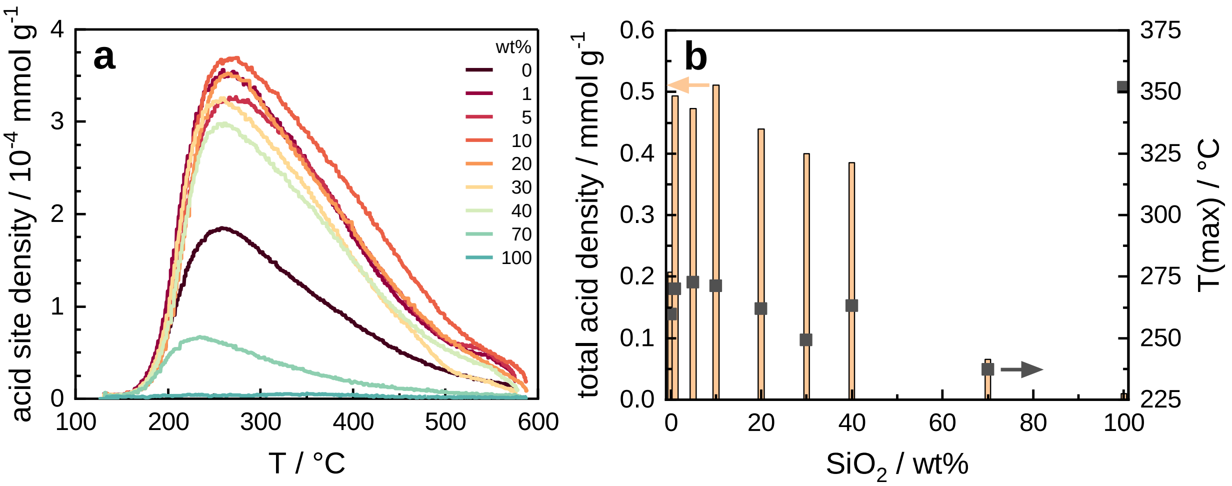

Figure S12: NH3-TPD curves (a) and from there derived total number of acid sites and maximum desorption temperature (b) for silica-alumina with varying silica content (in wt%).

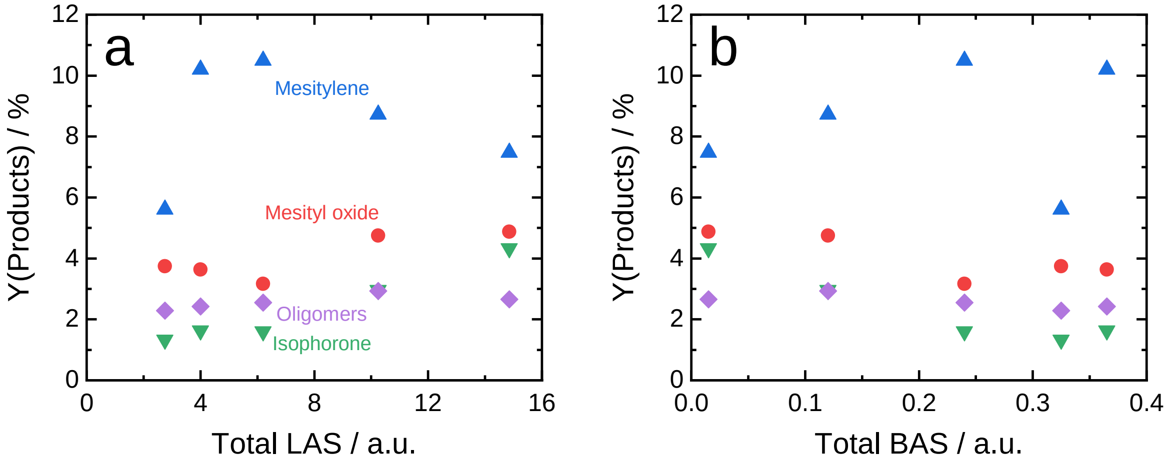

Figure S13: Product yields based on the total amount of Lewis acid sites (a) and Brønsted acid sites (b) measured by Nassreddine et al. via pyridine-desorption IR.[4]

References:

(1) Dettmer-Wilde, K.; Practical Gas Chromatography: A Comprehensive Reference, Springer Berlin / Heidelberg, Berlin, Heidelberg, **2014**.

(2) Reif, P.; Gupta, N. K.; Rose, M. Liquid phase aromatization of bio-based ketones over a stable solid acid catalyst under batch and continuous flow conditions. Catal. Commun. **2022**, 163, 106402. DOI: 10.1016/j.catcom.2022.106402.

(3) Sahoo, S. K.; Ray, S. S.; Singh, I. D. Structural characterization of coke on spent hydroprocessing catalysts used for processing of vacuum gas oils. *Appl. Catal., A* **2004**, *278* (1), 83–91. DOI: 10.1016/j.apcata.2004.09.028.

(4) Nassreddine, S.; Casu, S.; Zotin, J. L.; Geantet, C.; Piccolo, L. Thiotolerant Ir/SiO2–Al2O3 bifunctional catalysts: effect of support acidity on tetralin hydroconversion. *Catal. Sci. Technol.* **2011**, *1* (3), 408–412. DOI: 10.1039/c1cy00002k.