Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Improving the efficiency of the Diels-Alder process by using flow chemistry and zeolite catalysis

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^{1}H spectra were recorded on a Bruker Avance III Nanobay 400 MHz spectrometer at room temperature. The purity of the end products was additionally verified by GC on an Agilent 6980 Series gas chromatograph, equipped with an FID detector, using an Alltech EC-5 capillary column (30 m length x 0.25 mm i.d.; 0.25 µm film thickness) or by GC-MS, using an Agilent 6890 GC Plus apparatus, coupled to a quadrupole mass spectrometer 5973 MSD (Agilent Technologies) with electron ionization 70 eV and equipped with a DB-5 capillary column (30 m length x 0.25 mm i.d.; 0.25 µm film thickness). The TGA-DSC experiments were performed in a Sensys Evo TG-DSC (Setaram Instrumentation, France), operating in coupled TGA-DSC mode. High-purity oxygen was used to sweep the reactor volume at a rate of 20 ml/min. Zeolite samples, weighing approximately 5 mg, were put in an platinum crucible and mounted on the TGA balance inside the DSC furnace. The applied temperature scheme included a stabilising period of 5 min at 30°C, heating at 10 °C/min up to 800°C and cooling to 30°C. The specific surface area of the catalysts was measured by a N_2-sorption analyser (Quantachrome ASIQM 0002-4) at −196°C using the BET method, each sample was degassed at 200°C. Temperature programmed desorption (TPD) was used to determine the concentration of acid sites and heats of desorption of ammonia. These measurements were performed on a Micromeritics Autochem II 2920 apparatus equipped with a thermal conductivity detector (TCD). As pretreatment the catalyst was heated up to 230°C overnight to determine the dry weight of the catalyst. First, the sample was heated to 550°C (β=20°C min^{-1}) in helium to remove all physisorbed water species. Further the analysis gas (4%NH_3/96%He) flows through the sample and adsorbs on the acid sites due to a physisorption and chemisorption bounding. Hereafter, the sample was flushed at 100°C with pure helium to remove al physisorbed species. At last, the samples were heated up to 700°C to desorb all adsorbed molecules. The detector was calibrated using a known volume of ammonia. The concentrations of acid sites were calculated using the convolution method. The SEM analysis was performed on a Nova Nanosem 450 (FEI company), equipped with a circular backscattered detector (voltage of 5 kV). The magnification mentioned on the images are based on polaroid format.

Scanning Electron Microscopy

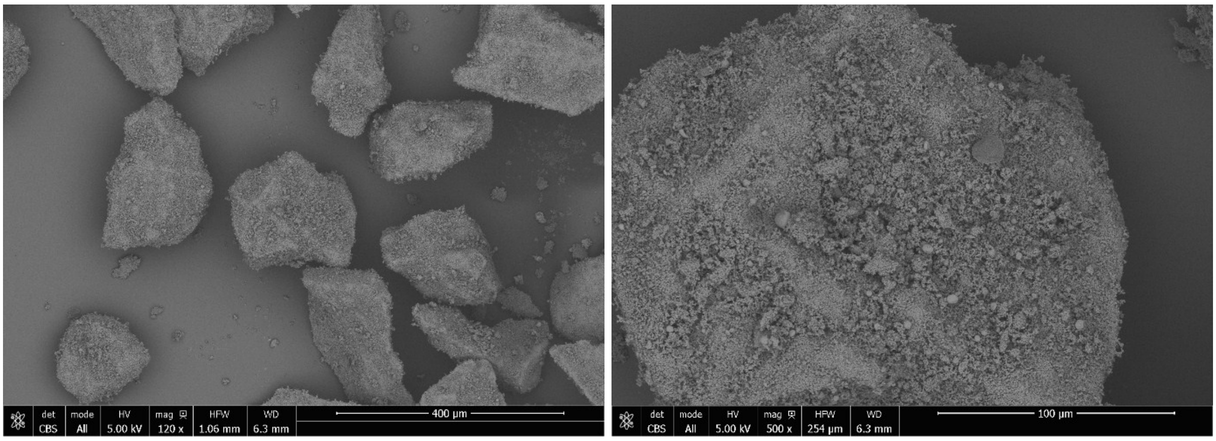

Figure S1 SEM images of fresh H-USY CBV 720 pellets

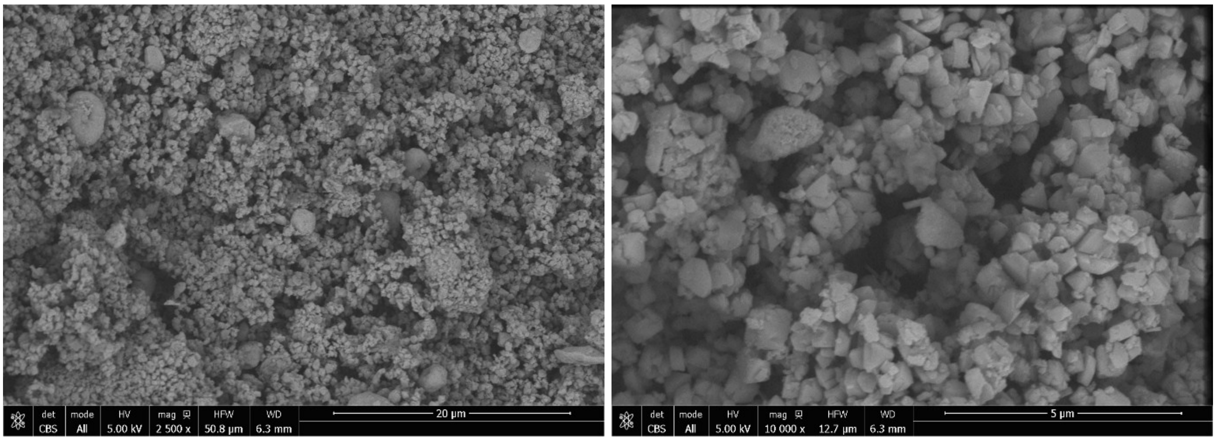

Figure S2 SEM images of the organisation of material in a H-USY CBV 720 pellet

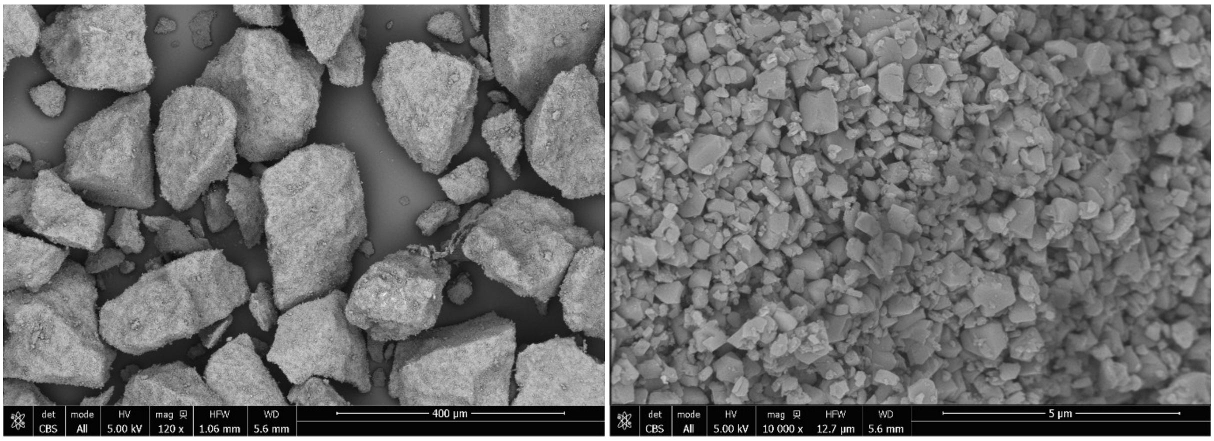

Figure S3 SEM images of used H-USY CBV 720 pellets in the continuous Diels-Alder process

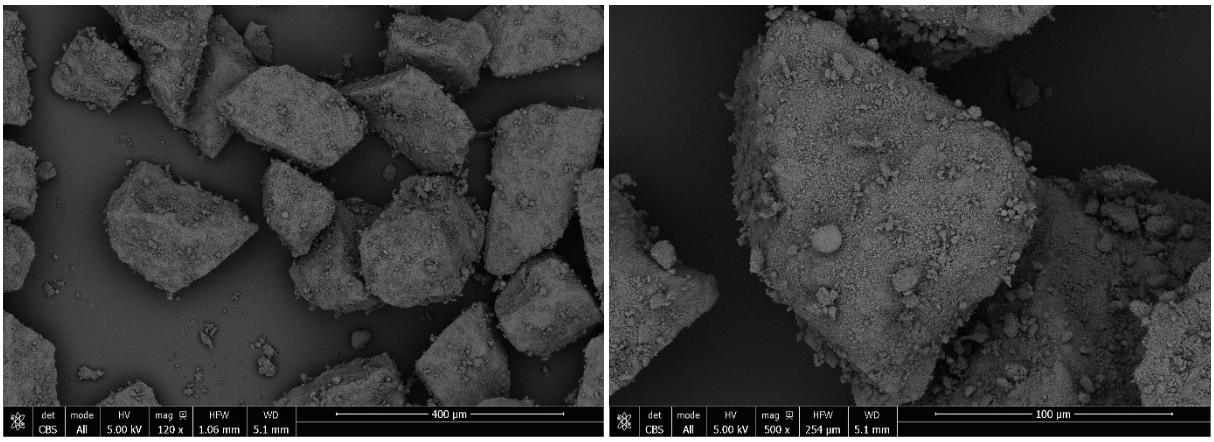

Figure S4 SEM images of fresh H-Beta CP814E* pellets

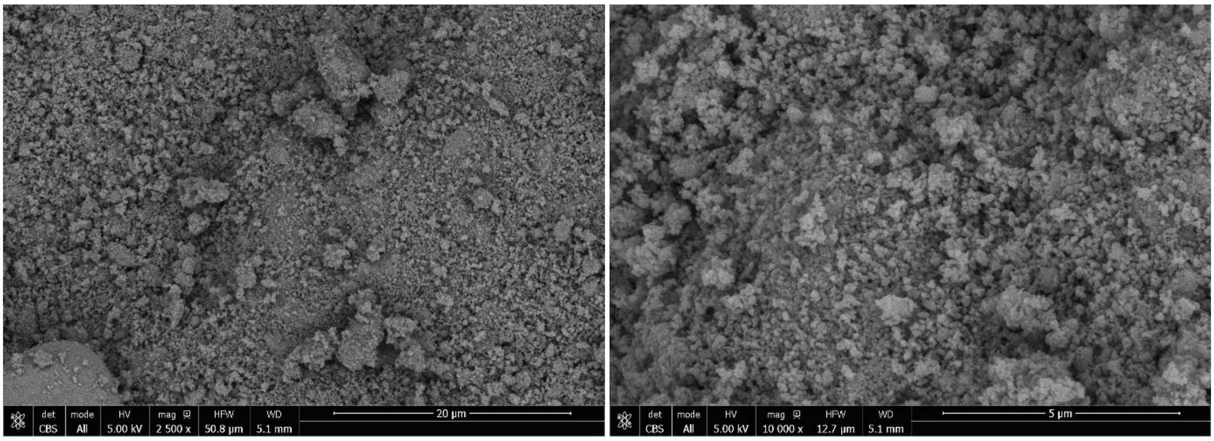

Figure S5 SEM images of the organisation of material in a H-Beta CP814E* pellet

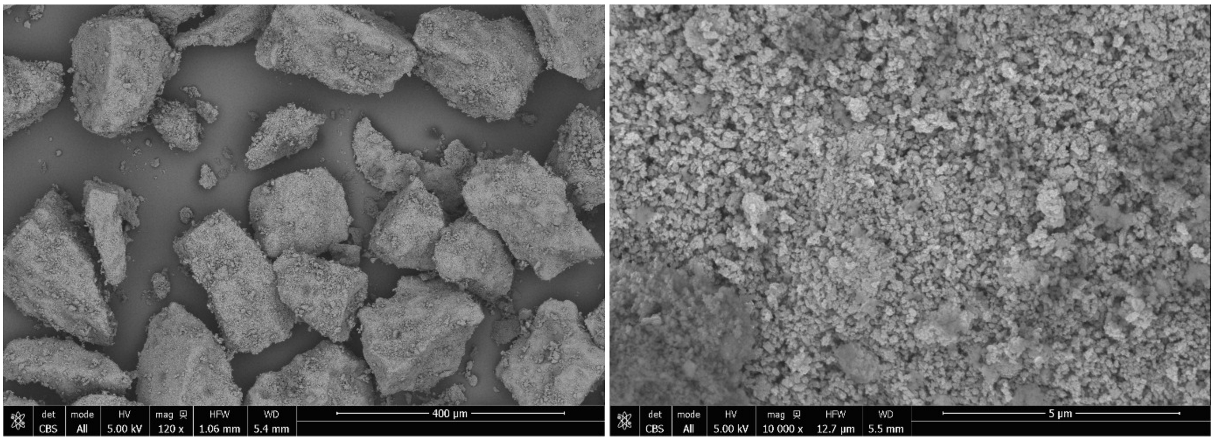

Figure S6 SEM images of used H-Beta CP814E* pellets in the continuous Diels-Alder process

Thermogravimetric analysis

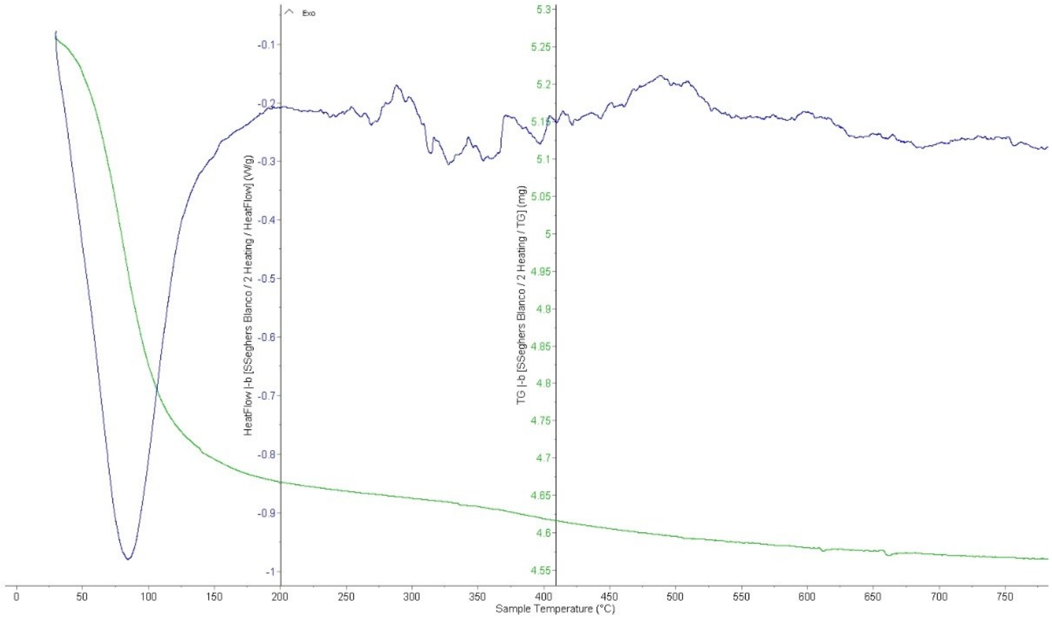

Figure S7 TGA analysis of CBV 720 powder (H-USY)

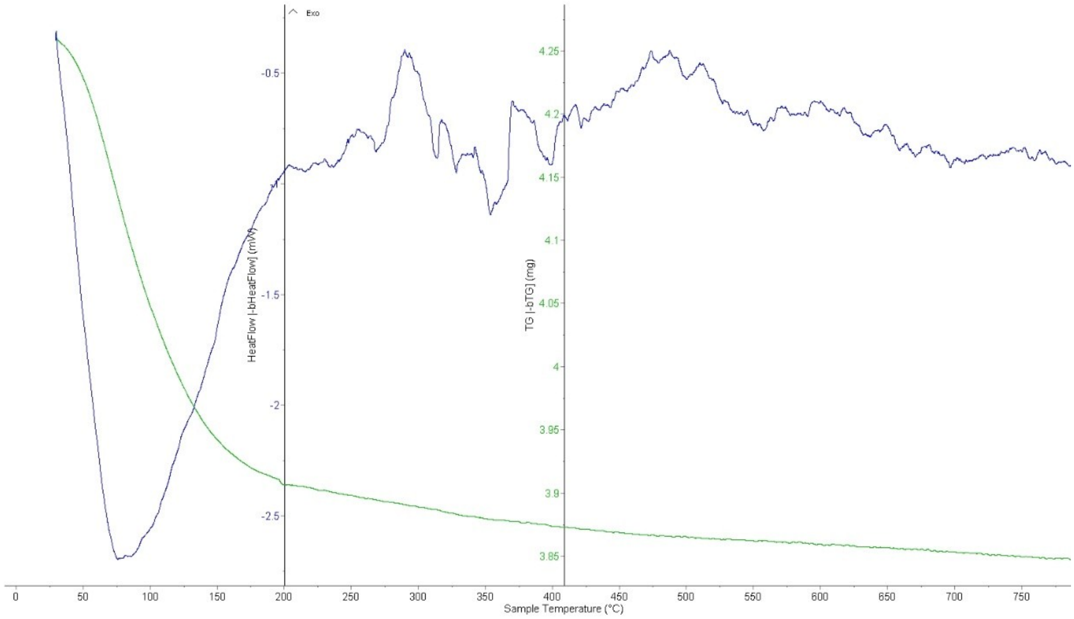

Figure S8 TGA analysis of CP814E* powder (H-Beta)

Typical batch procedure for the Diels-Alder reaction of cyclopentadiene and methyl acrylate

A 25 mL flask was equipped with a water condenser, a claisen piece and a nitrogen bubbler and the set-up was flame-dried. The flask was charged with 20 mL dry solvent and 0.13 g cyclopentadiene (1 equiv., 2 mmol, 0.1 M), 0.17 g methyl acrylate (1 equiv., 2 mmol, 0.1 M) and 40 mg (30 wt%) zeolite catalyst were added. The reaction mixture was brought to reflux temperature. Analysis was performed via integration of the methoxy-signals of MA and the endo- and exo-DA isomer in the ^{1}H-NMR spectrum of the crude reaction mixture.

Continuous flow procedure for the Diels-Alder reaction of cyclopentadiene and methyl acrylate

A 100 mL starting solution containing 0.5 M cyclopentadiene (1 equiv., 3.305 g, 50 mmol) and 0.5 M methyl acrylate (1 equiv., 4.304 g, 50 mmol) in (dry) dichloromethane was prepared. The reagent solution was stored in an ice bath to avoid any (side) reaction outside the reactor environment and was placed under an N_2-pressure, using a pressurisation module of the commercially available Africa flow system (Syrris). After thoroughly rinsing the X-Cube™ flow reactor with (dry) dichloromethane, the catalyst cartridge (CatCart®) was manually loaded with zeolite (particle fraction 125-200 µm). Next, the CatCart® was added in the set-up, as described in Section 2.2 and presented in Figure 1. The system was rinsed with the reagent solution at 1 mL/min, 30 bar and 100 °C. After 10 min, the flow rate was reduced to the required flow rate. A first sample was collected after one hour and analyzed via integration of the methoxy-signals of MA and the endo- and exo-DA isomer in the ^{1}H-NMR spectrum of the crude reaction mixture. In this way, the process was monitored for 7 h. The end products were isolated as a mixture of endo- and exo-isomers via mild evaporation. The obtained norbornene derivatives are known compounds and spectral data corresponded with literature data.[1]

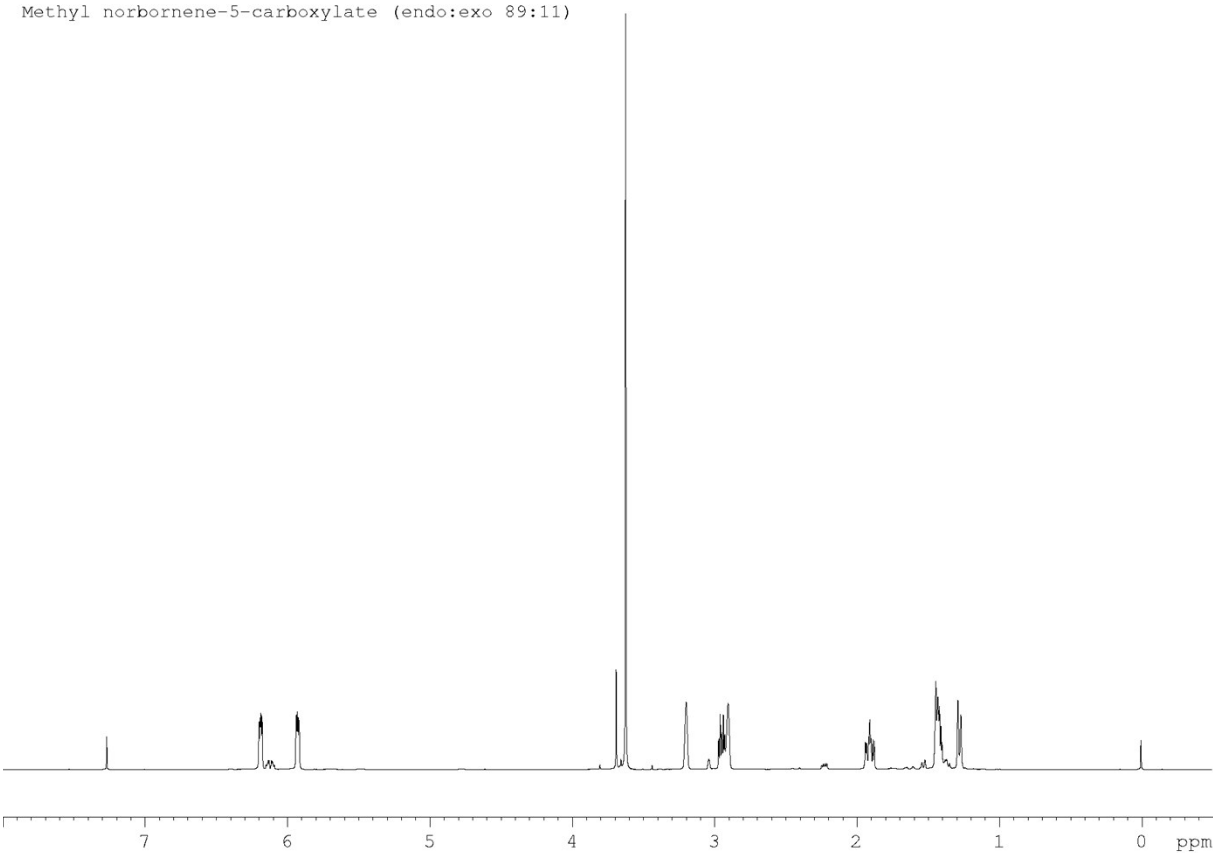

Figure S9 1H-NMR spectrum of the isolated mixture of methyl norbornene-5-carboxylate isomers

References

1. (a) Kanao, M.; Otake, A.; Tsuchiya, K.; Ogino, K., Stereo-Selective Synthesis of 5-Norbornene-2-exo-carboxylic Acid - Rapid Isomerization and Kinetically Selective Hydrolysis. *Int. J. Org. Chem.* **2012,** *2*, 26-30; (b) Okamoto, A.; Snow, M. S.; Arnold, D. R., Radical Ions In Photochemistry.17. Photosensitized (Electron-Transfer) Carbon-Carbon Bond-Cleavage Of Radical Cations - The Diphenylmethyl System. *Tetrahedron* **1986,** *42* (22), 6175-6187; (c) Vygodskii, Y. S.; Shaplov, A. S.; Lozinskaya, E. I.; Filippov, O. A.; Shubina, E. S.; Bandari, R.; Buchmeiser, M. R., Ring-opening metathesis polymerization (ROMP) in ionic liquids: Scope and limitations. *Macromolecules* **2006,** *39* (23), 7821-7830.