Electronic Supporting Information (ESI)

p-Xylene from 2,5-dimethylfuran and acrylic acid using zeolite in continuous flow system

Jose Alirio Mendoza Mesa[a,b], Francesco Brandi[a], Irina Shekova[a], Markus Antonietti[a], Majd Al-Naji[a]*

[a] Max Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, 14476 Potsdam, Germany

[b] Laboratorio de Catálisis Heterogénea, Universidad Nacional de Colombia, 11001 Bogotá, Colombia

Experimental section

Materials

Beta zeolite in H-form (150, 90 and 25) were supplied by *Clariant*. The H-form ZSM-5(280) and Y(80) were obtain from *Zeolyst*. 2,5-Dymethilfurane (>99%), Acrylic Acid (>99%), *p*-xylene (>99%); 2,5-dimethyl benzoic acid (>98%), hexadione (98%), nitric acid (>99%), Formic Acid (>95%) and sodium hydroxide(98%) were purchased by Sigma Aldrich. Ammonium Nitrate (>98) and Cetyltrimethylammonium Bromide (99%) was provided by Across Organics. *n*-heptane (>99%) was obtained from VWR. Acetonitrile (99.9%), Sodium Nitrate (>99.5) has been acquired from Merck.

Catalyst preparation

Hierarchization

The hierachization of Beta(150) was performed using aqueous alkaline solution (0.2 M) of NaOH with (0.01 M) Cetyltrimethylammonium Bromide (CTAB) as a soft templating agent. The zeolite was dispersed in the solution (30 cm^3 g$_{zeolite}^{-1}$) and heated at 338 K for 30 min while stirring and using a reflux system to recover the solvent. The resulting slurry was quenched with ice-water, and treated with a four step procedure consisting of i) centrifugation to isolate the solid (30 minutes at 2000 rpm); ii) removal of treatment solution, *i.e.* NaOH and CTAB, via extensively washing with deionized H$_2$O (almost 20 cm^3 g$_{zeolite}^{-1}$); iv) Centrifugation to separate the solid (30 minutes at 2000 rpm); v) drying in air oven at 373 K for almost 12 h. The resulting materials were converted into the H-form by two consecutive ion exchanges in aqueous NH$_4$NO$_3$ solution (1M). The zeolite was dispersed in the solution (100 cm^3 g$_{zeolite}^{-1}$) and heated at 338 K for 8 h min while stirring and using a reflux system to recover the solvent. After the treatment, the solution was quenched and treated with the same four-step process described previously. Finally, the resulting material has been calcined at 823 K under static air (heating ramp 5 K min^{-1} to 823 K and maintain for 5 h).

Dealumination

Dealumination acid treatment over Beta(150) were performed using an acidic solution (2M) of HNO$_3$. The zeolite was dispersed in the acidic solution (30 cm^3 g$_{zeolite}^{-1}$) and heated at 353 K for 1h min while stirring and using a reflux system to recover the solvent. After the treatment the materials has been quenched and processed with the same four-step procedure described above.

Ion Exchange with Na

Beta zeolite was converted into the partial Na-form by ion exchange in aqueous NaNO$_3$ solution (0.5 M). The Beta zeolite was dispersed in the solution (30 cm^3 g$_{zeolite}^{-1}$) and heated up to 353 K for 1 h min while stirring and using a reflux system to recover the solvent. After the treatment the materials has been quenched and processed with the same four-step procedure described above.

Catalyst characterization

NH$_3$ – Temperature programmed desorption (TPD)

The total acid sites density for all utilized catalyst was characterized via ammonia temperature-programmed desorption (NH$_3$-TPD). All measurements were performed using AMI-300 equipped with thermal conductivity detector (TCD) from Altamira Instrument. In each measurement, 0.05 g of catalyst was placed between two layers of quartz wool in the measurement cell (quartz U-tube). primarily, the sample was treated at 393 K in a flow He for 1 h. Afterwards, saturation of the catalyst with NH$_3$ at 323 K was applied by flowing NH$_3$ (20%) over the sample for 5 h. Then, the non-adsorbed NH$_3$ was removed by flowing He (100%) over the sample for 30 min. To ensure a complete saturation of the samples, 20 pulses (509 μL each) of NH$_3$ (20%) in He (80%) over the sample at 323 K was pulsed. Finally, the NH$_3$ desorption profile was recorded by increasing the temperature from 323 K to 923 K with 10 K min^{-1} with dwell of 30 min at 923 K.

Elemental analysis

Si/Al molar ratios were determinated by Inductively Coupled Plasma Optical emission Spectroscopy (ICP-OES) using Optima 8000 ICP- ES from Perkin Elmer. Prior the analysis, the samples (0.01 g) were grinded finely and digested a 500 µL solution consisting of HCl (333 µL) and HNO_3 (167 µL) for 12 h at room temperature.

X-Ray diffraction

Powder XRD measurements were performed on a Bruker D8 diffractometer. The X-ray source was Cu-Kα(λ=0.154 nm) equipped with a NaI scintillation counter-Scinti-Detector. The diffraction data was recorded in the 5-55 2θ range with an angular step of 0.05 and acquiring time of 2 s per step. Prior to the analysis the samples were finely grinded.

N_2-sorption

N_2-sorption measurements were performed at 77 K using a Quantachrome Quadrasorb SI porosimeter. Prior the analysis the samples have been degassed for 20 h at 100 mbar and 423 K. The quantification of the specific pore volumes (Vi) and specific surface areas (Si) for the different pore types, was determined by application of the Non Local Density functional theory(NLDFT) model on the adsorption branch of the isotherm.[1]

Thermogravimetric analysis (TGA)

TGA measurement has been performed using a Thermo Microbalance TG 209 F1 Libra (Netzsch, Selb, Germany). A Pt crucible was used for the measurement of 10 mg of samples under a flow of synthetic air of 10ml/min and a purge flow of 10ml/min. The samples have been heated with heat rate of 10 K min^{-1} to 1183 K. Data of both measurements have been recorded and analyzed by the Proteus (6.1.0) and Quadstar (7.03, MID modus) software package.

Transmission electron microscopy (TEM)

The morphology of the Beta(150) and Hi-Beta(150) was investigated using TEM. The sample was prepared by dispersing (0.05 g) in ethanol in an ultrasonic bath for 10 min. Finally, the sample was placed onto a carbon-coated copper grid and dried at room temperature. The images were taken using an EM 912 microscopy (Omega/Carl-Zeiss Oberkochen) operating at 120 kV.

Experimental setup and reaction procedure

Figure S1A. Experimental setup used for synthesis of *p*XL.
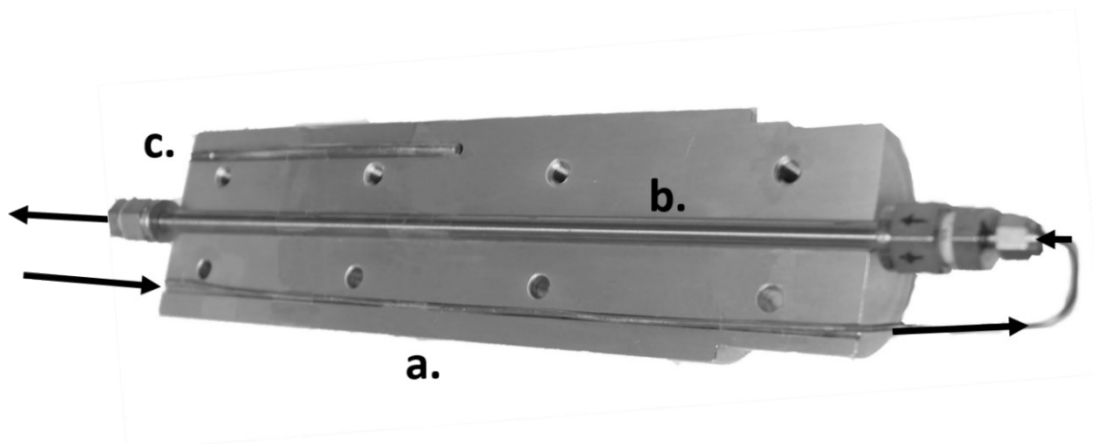
Figure S1B. Heat-transfer unit comprising of pre-heating unit (a), tubular reactor (b) and thermocouple (c).[2,3]

Prior the reaction, the catalyst was dried in static air at 393 K for 1 h and calcined at 773 K for 5 h with heating ramp of 5 K min⁻¹. To ensure a homogeneous flow of the reactant through the catalyst bed during the experiment, as well as avoiding the pressure drop and clogging of the system, The catalyst in powder form were pressed using hydraulics press (CARVER 3851CE) with 10 metric ton. Afterwards, the zeolite has been crushed and sieved in the range 500-1000 μm. Experiments were conducted with around 2.0 g of zeolite; silicon carbide particles has been used as filler at the entrance and exit of the reactor, to ensure a fixed position of the catalyst.

 In a typical experiment, the 2,5-Dimethylfuran (DMF) upgrading to *p*-xylene (*p*XL) in presence of acrylic acid (AA) was studied in a homemade continuous-flow fixed bed reactor (**Figure S1**).[2,3] A solution of DMF (0.3 M) with AA (0.7 M) in *n*-heptane was supplied to the reactor by (**A**) HPLC pump equipped with a pressure sensor (Jasco PU-2080 plus) through a stainless steel tubing (1/16" of inner diameter from *Swagelok*), (**B**) a heating unit consisting of oven equipped with heat controller (*Model 4848 from Parr Instrument Company*). To ensure an efficient heat transfer an aluminum cylinder with three different holes was designed to be placed inside the oven (**Figure S1B**). The aluminum cylinder consist of: 1/16" hole as pre-heating unit (**Figure S1B-a**) to heat the reactant to the desired reaction temperature before its get contact with catalyst bed, 1/4" hole to place the fixed-bed reactor stainless steel tubular reactor from *Swagelok* with

dimensions of inner diameter (ID) = 4.6 mm and length (l) = 25 cm, (**Figure S1B)**, and a third hole for the thermocouple (Model A472E5 from Parr Instrument Company) *viz.* **in Figure S1B-c.** The sampling unit (**Figure S1A-C.**) was equipped with a back-pressure regulator (Swagelok SS-RL4M8F8-EP) to control the system pressure which was set to 3.0-3.5 MPa.

The residence time (τ) has been defined as V/Q, where is (V) is the reactor volume and (Q) is the flow rate. The empty reactor volume was calculated based on the reactor dimensions (inner diameter = 4.6 mm, outer diameter = 1/4" and length = 25 cm), lead to a reactor volume of 4.15 cm^3. However, the reactor volume in the presence the quartz wool was found 3.04 cm^3, which has been used to calculate the actual residence time of the reaction.

Caution 1: The catalyst regeneration was conducted by thermal treatment of the spent catalyst at 823 K with 10 K min^{-1} for 5 h in air.

Reactants and products analysis and quantification

After the reactions, the products were identified via Gas chromatography coupled with Mass spectroscopy (GC-MS) from Agilent model 6890N coupled with an Agilent 5975 MSD as mass spectrometer detector, equipped with a HP-5MS Ultra Inert column from Agilent (model: USR577054H). The method has been set with a retention time of 22 min and injection volume of 0.2 μL and He as carrier gas. The injection mode has been selected as Split with a split ratio of 50. The temperature program has been set as following: start from 323 K and maintained for 2 min, then elevated to 523 K with heating rate of 10 K min^{-1}. The MS detector has been set to scan between 50 and 250 m/z. The mass spectra of the compounds were analyzed integrating the peak area using the MSD ChemStation E.02.02.1431 Software and comparing with the NIST 05 mass spectral database.

Quantitative analysis was carried using a HPLC Agilent 1200 series equipped with a quaternary pump, a C18 column (C18 Hypersil Gold Column Selectivity LC Series, 5 mm 250 $\times$ 4.6 mm) and Diode array-detector (DAD). The analysis program was set to 18 min at 308 K using 3 μL of injection volume and 0.1 wt.% with eluent flow of 1.2 cm^3 min^{-1}. To ensure the complete peak resolution a non-isocratic elution of formic acid (FA 0.1 wt.% in water) and acetonitrile (ACN) has

been selected, consisting of three step: i) FA/ACN 80/20 vol. ratio for the first 2 min; ii) non-isocratic gradient from 80/20 FA/ACN to pure ACN between the 3rd to the 7th min and maintained ACN for 5 minutes; iii) the initial 80/20 FA/ACN vol. ratio has been reset. In order to maximize the sensitivity toward each compound DAD detector has been set to the wavelength of the absorbance maximum of each compound, *i.e.* 233 nm for 2,5-dimethylfuran (DMF) and 262 nm for *p*-xylene (*p*XL), acrylic acid (AA) and 2,5-dimehyl benzoic acid (DMBA).

The reactants and products (DMF, AA, *p*XL and DMBA) were identified comparing the retention time with standard substances, *i.e.* 2.74 min for AA, 8.97 min for DMF, 8.1 min for DMBA and 9.6 min for *p*XL. The molar concentration of the reactants and product was calculated from the integration area of the peaks referred to the calibration curve made using standard compounds,

The reactants conversion X_r, were calculated according to the following equations:

$$X_{r,t} = \left(\frac{n_{r,to} - n_{r,t}}{n_{r,to}} \right) x100\%$$

Where $n_{r,t0}$ and $n_{r,t}$ indicates respectively the molar concentration of the reactant at the initial time (t_0) and at a given time t. The products yields were calculated according to the following equations:

$$Y_{p,t} = \left(\frac{n_{p,det}}{n_{r,t}} \right) x100\%$$

Where $n_{p,det}$ represent the detected molar concentration of the product.

Caution 2: in all the catalytic experiments, DMF as it is the limited reactant was used to calculate the yield of *p*XL and DMBA. Only in the experiment that DMF/AA molar ratio is 1.1, AA was used to calculate the yield as it is limited reactant.

The Turn-Over Frequency of the formation of *p*-xylene (TON) has been calculated according the following equation:

$$TOF = \frac{TON}{t_r}$$

where t_r represent the residence time inside the reactor expressed in h and TON indicates the turn-over number, calculated as follow:

$$TON = \frac{N_{pXL}}{N_{Acid\ sites}} = \frac{n_{pXL} \cdot V_{React}}{H^+_{Density} \cdot M_{Cat}}$$

Where N_{pXL} indicates the mole number of *p*-xylene calculated from the detected *p*-xylene concentration n_{pXyl} and the reactor volume V_{React}. Similarly, $N_{Acid\ sites}$ indicates the atomic mole number of acidic site, calculated from the NH_3-TPD acidic site density , $H^+_{Density}$, and the catalyst mass, M_{cat}.

Additionally, the space time yield of *p*-Xylene (STY_{pXL}) , expressed in $kg_{pXL}\ h^{-1}\ kg_{cat}^{-1}$, has been calculated from the p-Xylene flow rate (Q_{pXL}) ,according to the following equation:

$$STY_{pXL} = \frac{Q_{pXL}}{M_{Cat}} = \frac{Y_{pXL} \cdot m_{pXL} \cdot n_{r,to}}{M_{Cat} \cdot Q_{Educt}}$$

Where Y_{pXL} and $n_{r,to}$ indicates respectively the *p*XL yield and the reactant concentration calculated as above-reported. Moreover, m_{pXL}, M_{cat} and Q_{Educt} represent ,respectively, the molecular mass of *p*XL (0.106 kg mol^{-1}), the total mass of catalyst (expressed in kg) and the reactant flow (expressed in L h^{-1}).

Results and discussion
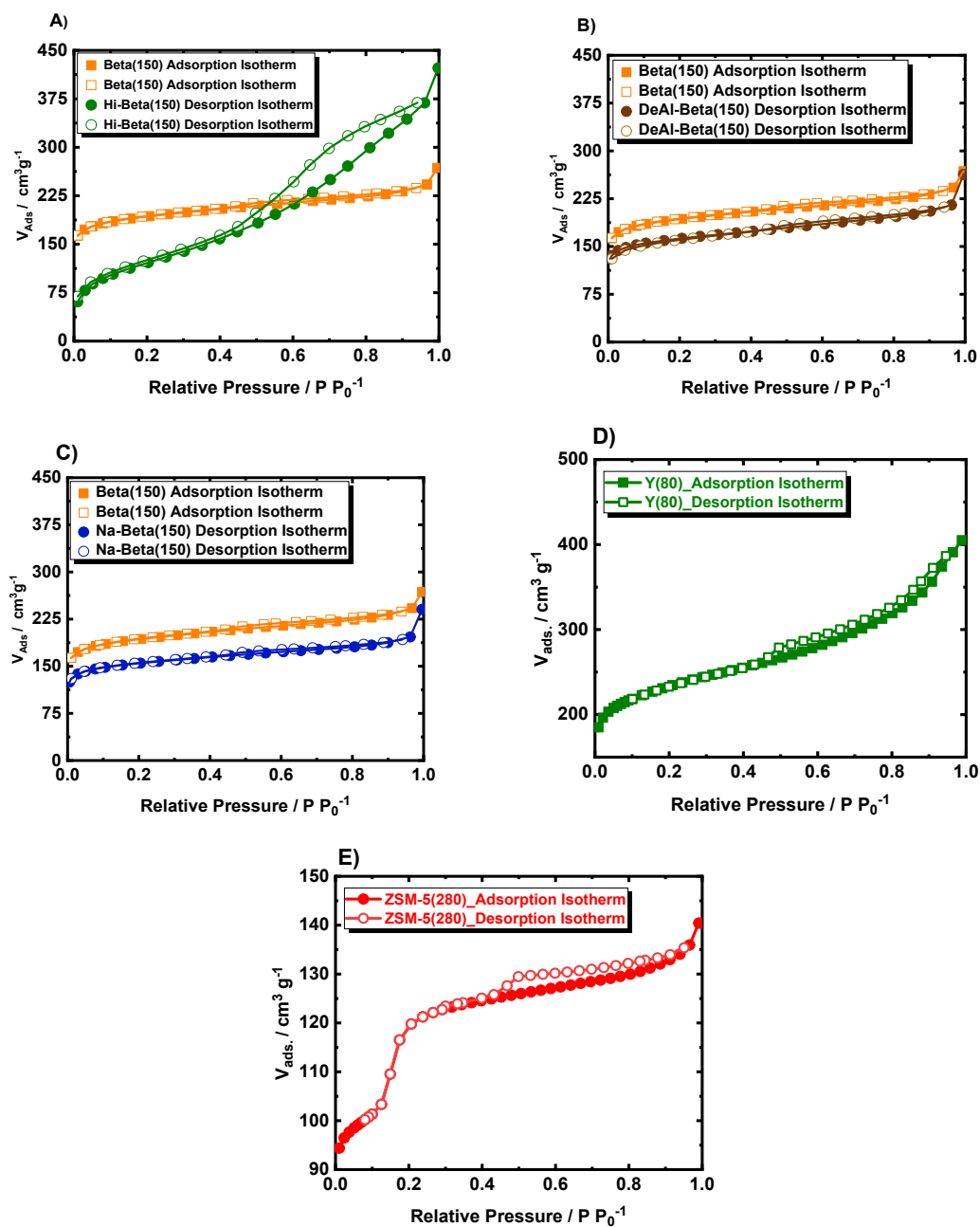
Figure S2. N$_2$-sorption isotherms at 77 K of A) Beta(150) and Hi-Beta, B) DeAl-Beta(150), C) Na-Beta(150), D) Y(80) and ZSM-5(280).
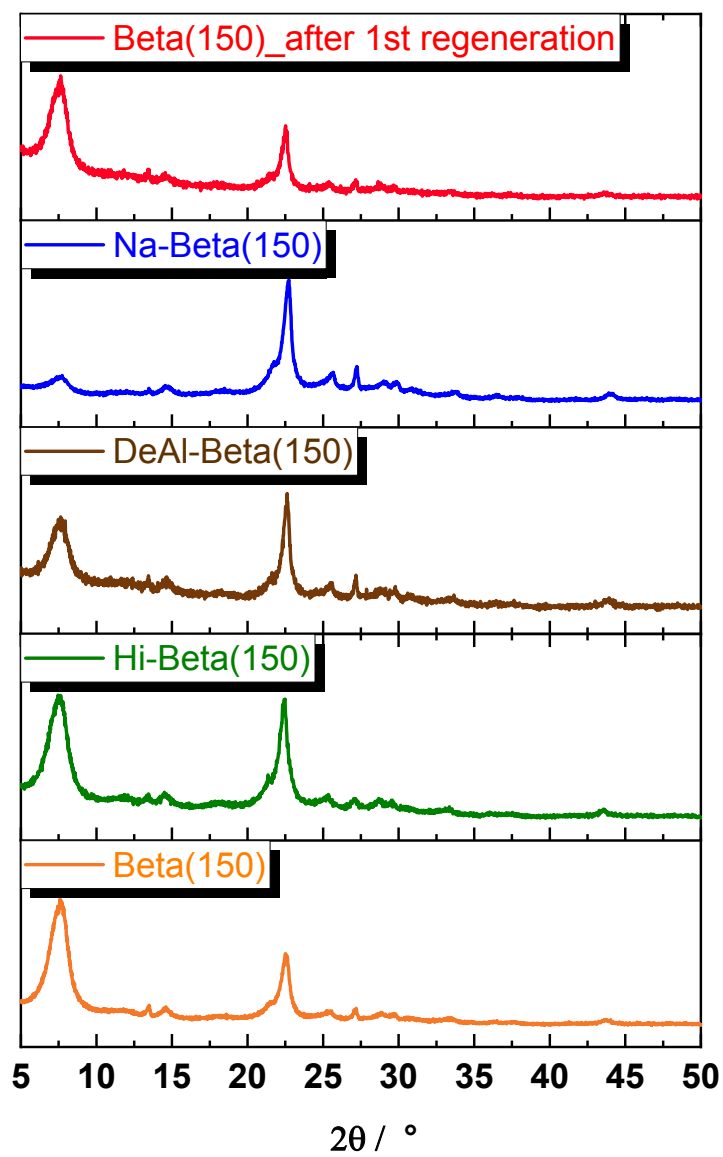
Figure S3. XRD patterns for Beta(150), Hi-Beta(150), DeAl-Beta(150), Na-Beta(150) and after 1st regeneration of Beta(150).
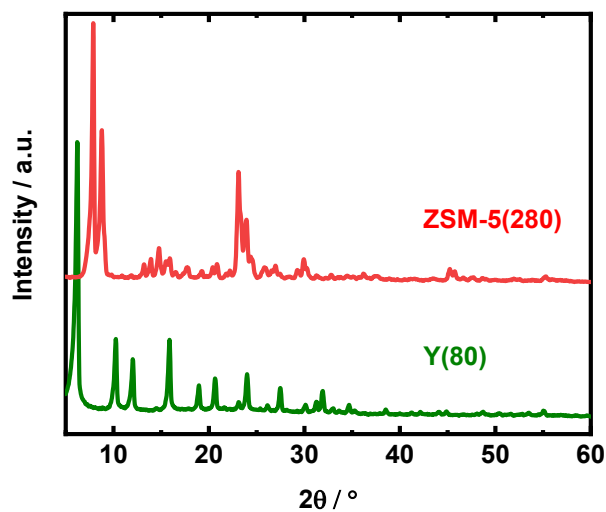
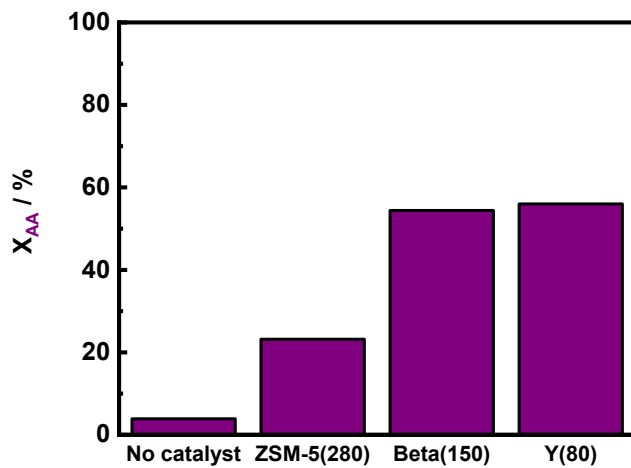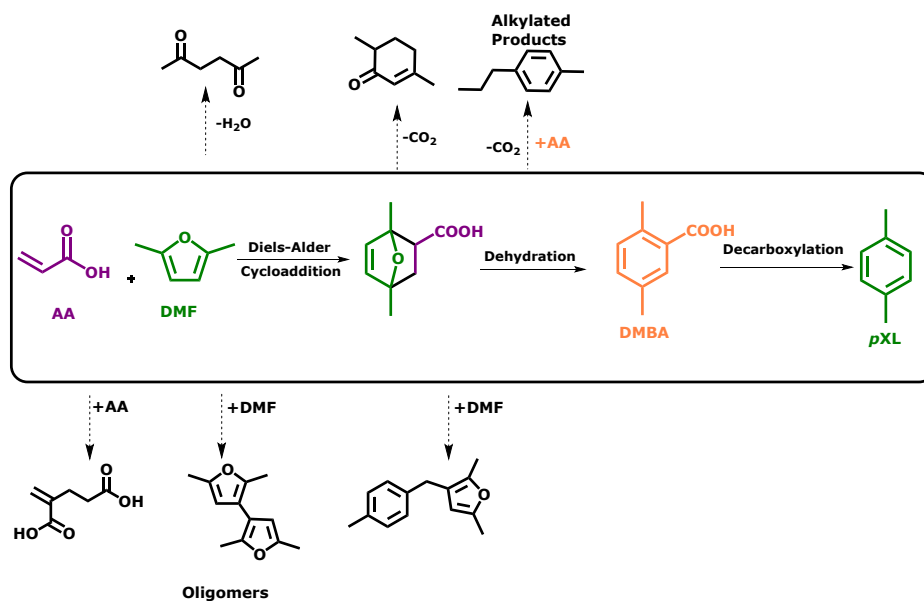**Figure S4**. XRD patterns for Y(80) and ZSM-5(280).

Figure S5. AA conversion (X_{AA}) after 2 h of time on stream as a function of different catalyst (no catalyst, ZSM5-(280), Beta(150) and Y(80); reaction conditions: c_{DMF} = 0.3 M, c_{AA} = 0.7 M, T = 473 K, m_{cat} = 2 g, Q_{educt} = 0.3 cm^3 min^{-1}, $V_{reactor}$ = 3.04 cm^3, p_{system} = 3 MPa and τ = 10.1 min.

Scheme S1. The reactions involved in the synthesis of *p*XL starting to DMF in the presence of AA. The choice of the proper zeolite structure and optimal reaction conditions makes the frame highlighted the preferential pathway. Tri-mode selectivity is made by reactant, intermediary and product selectivity. Furthermore, proposed side reactions that caused the deactivation of the catalyst are shown above and below the highlighted preferential pathway.
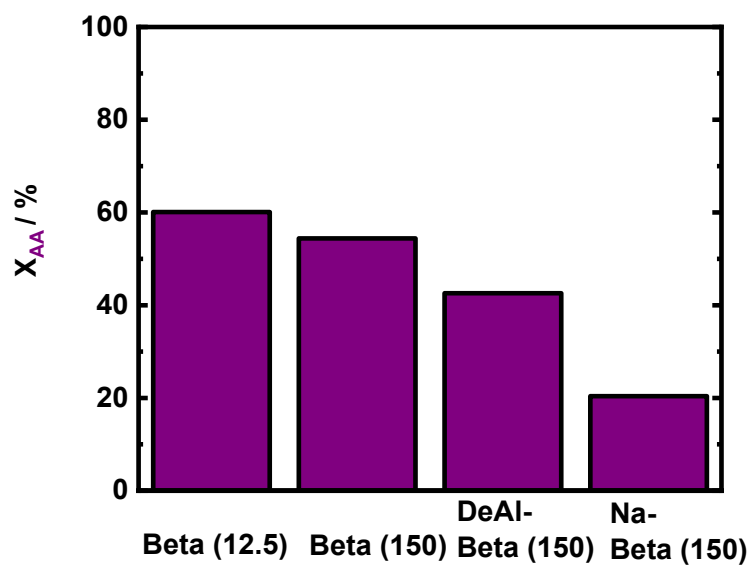
Figure S6. AA conversion (X_{AA}) after 2 h of time on stream over different Beta zeolite (Beta(12.5), Beta(150), DeAl-Beta(150) and Na-Beta(150); reaction conditions: c_{DMF} = 0.3 M, c_{AA} = 0.7 M, T = 473 K, m_{cat} = 2 g, Q_{educt} = 0.3 cm^3 min^{-1}, $V_{reactor}$ = 3.04 cm^3, p_{system} = 3 MPa, and τ = 10.1 min.
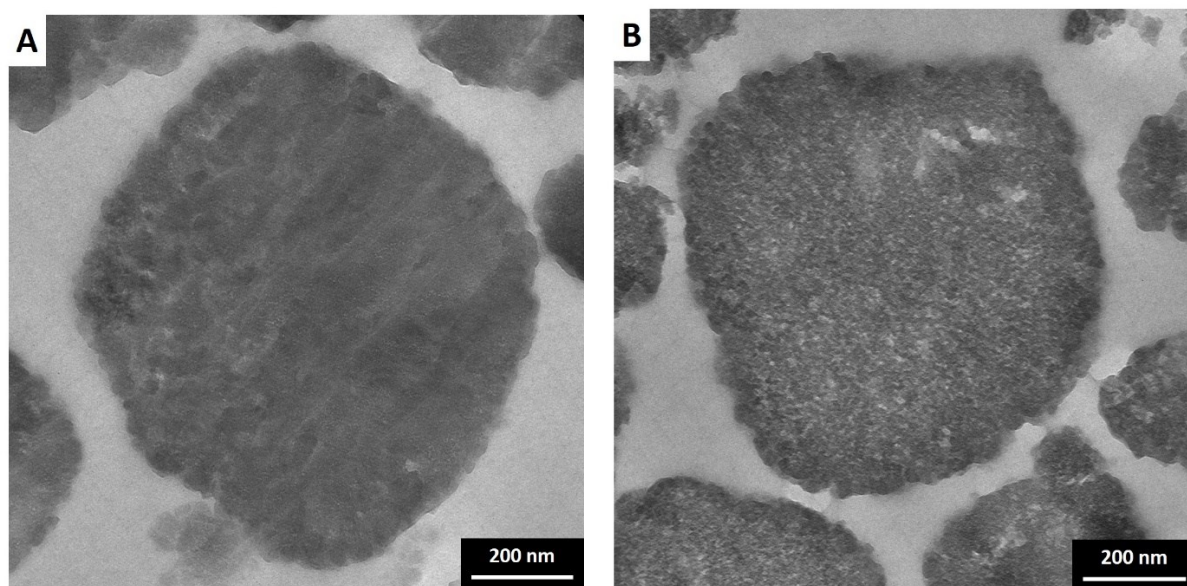
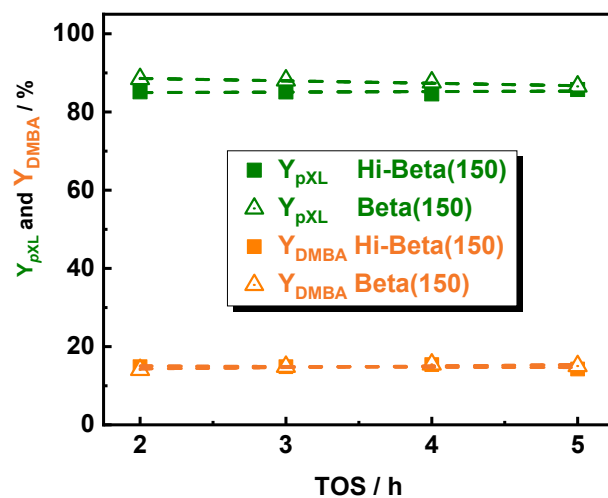

Figure S7. TEM images for Beta(150) and Hi-Beta(150).

Figure S8. *p*XL and DMBA yield ($Y_{pXL \text{ and }} Y_{DMBA}$) for Beta(150) and Hi-Beta(150); reaction conditions: c_{DMF} = 0.3 M, c_{AA} = 0.7 M, m_{cat} = 2.0 g, $Q_{reactant}$ = 0.3 cm^3 min^{-1}, $V_{reactor}$ = 3.04 cm^3, $T_{reaction}$=473K, p_{system} = 3 MPa and τ = 10.1 min.
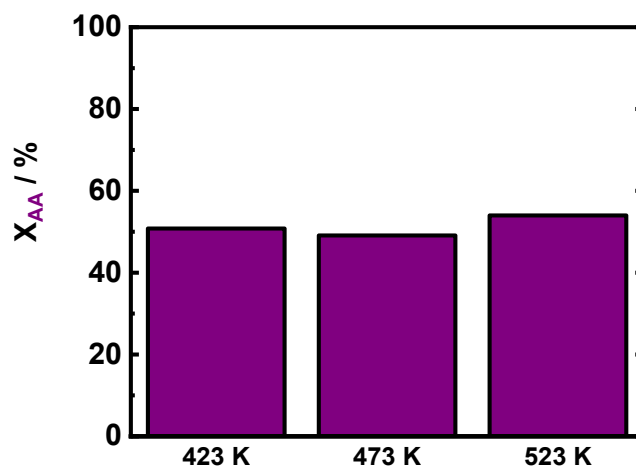
Figure S9. AA conversion (X_{AA}) after 2 h of time on stream as a function of reaction temperature (423 K, 473 K and 523 K); reaction conditions: c_{DMF} = 0.3 M, c_{AA} = 0.7 M, m_{cat} = 2 g, Q_{educt} = 0.3 cm^3 min^{-1}, $V_{reactor}$ = 3.04 cm^3, p_{system} = 3 MPa and τ = 10.1 min.
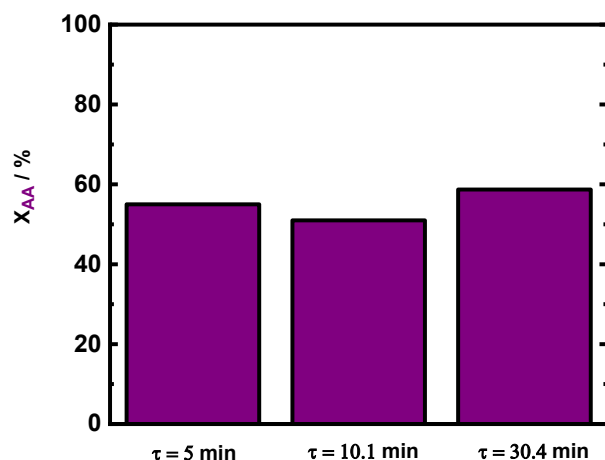
Figure S10. AA conversion (X_{AA}) over Beta(150) after 2 hours of time on stream as a function of residence time (τ); reaction conditions: c_{DMF} = 0.3 M, c_{AA} = 0.7 M, T = 473 K, m_{cat} = 2 g, Q_{educt} = 0.6 cm^3 min^{-1}, 0.3 cm^3 min^{-1} and 0.1 cm^3 min^{-1}, $V_{reactor}$ = 3.04 cm^3, p_{system} = 3 MPa and τ = 5.0 min, 10.1 min and 30.4 min.
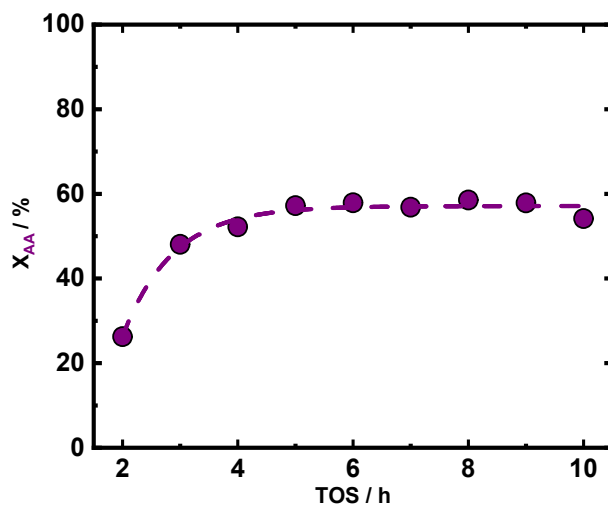

Figure S11. AA conversion (X_{AA}) over Beta(150) as a function of time on stream (TOS) for fresh Beta(150) after two regeneration steps; reaction conditions: c_{DMF} = 0.3 M, c_{AA} = 0.7 M, m_{cat} = 2 g, Q_{educt} = 0.3 cm^3 min^{-1}, $V_{reactor}$ = 3.04 cm^3, p_{system} = 3 MPa, and τ = 10.1 min.
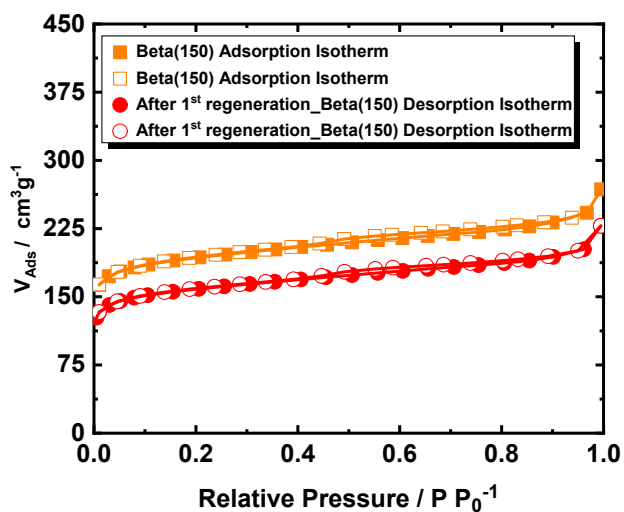
Figure S12. N$_2$-sorption isotherms for Beta(150) and after 1st regeneration of Beta(150).
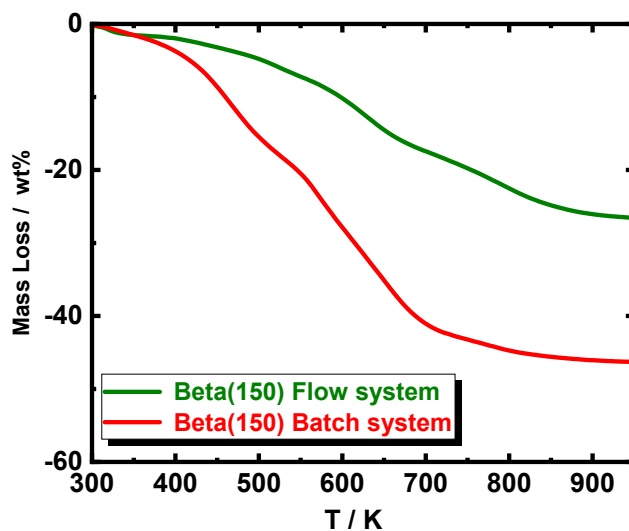

Figure S13. TGA analysis of spent Beta(150) zeolite after 8 hours in continuous flow system and batch reactor. Flow reactor and Batch reactor:; reaction conditions in continuous flow system: c_{DMF} = 0.3 M, c_{AA} = 0.7 M, T = 473 K, m_{cat} = 2 g, Q_{educt} = 0.3 cm^3 min^{-1}, $V_{reactor}$ = 4.15 cm^3, p_{system} = 3 MPa, and τ = 10.1 min; reaction conditions in batch reactor: c_{DMF} = 0.3 M, c_{AA} = 0.7 M, T = 473 K, m_{cat} = 2 g, n = 400 rpm, p = 3 MPa of N$_2$.
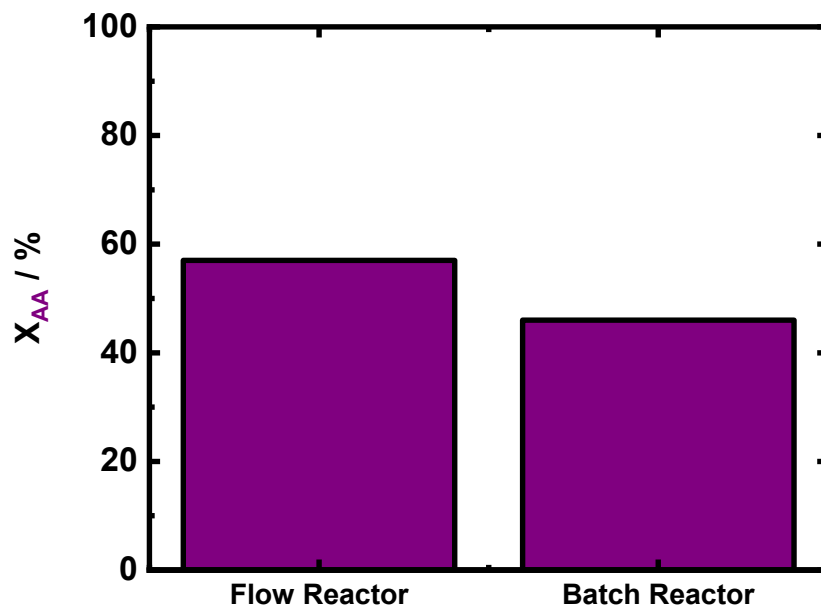
Figure S14. AA conversion (X_{AA}) over Beta(150) after 8 hours in continuous flow system and batch reactor; reaction conditions in continuous flow system: c_{DMF} = 0.3 M, c_{AA} = 0.6 M, T = 473 K, m_{cat} = 2 g, Q_{educt} = 0.3 cm^3 min^{-1}, $V_{reactor}$ = 4.15 cm^3, p_{system} = 3 MPa, and τ = 10.1 min; reaction conditions in batch reactor: c_{DMF} = 0.3 M, c_{AA} = 0.6 M, T = 473 K, m_{cat} = 2 g, n = 400 rpm, p = 3 MPa of N$_2$.

References

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