

The role of Beta zeolites in the selective single O-demethylation of alkyl-syringols to alkyl-methoxycatechols, a novel polymer building block class

Supporting Information

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Chemicals and materials

4-Methyl syringol (**MSyr** or 2,6-dimethoxy 4-methylphenol) ($\geq 97\%$), syringol (**Syr**) (99%), magnesium sulphate ($>99.5\%$), ammonium oxalate monohydrate ($>99.5\%$), 2-*iso*-propylphenol ($>98\%$), *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA, $>98.5\%$), benzyltriethylammonium bromide (TEBAC) (99%), Epichlorohydrin (99%), HCl (37%), Di-amino isophorone (IPDA) ($\geq 99\%$), NaOH (97%), and anhydrous pyridine (99.8%) were purchased from Sigma Aldrich. 4-Methyl , 5-methoxy catechol (**MMC**) (99%), 4-methyl gallol (**MGal** or 5-methylbenzene-1,2,3-triol)(99%), and 4-propyl syringol (**PSyr**) (99%) were provided from Beijing chemicals. Ethyl acetate (99.5%), was ordered from Acros Organics. Dichloromethane (DCM, $>99\%$) and niobium(V) oxalate hydrate were purchased from Fischer Chemical Ltd. Sodium hydroxide (NaOH, 98 wt %) was supplied by Beijing Chemical Reagent Company. ZSM-5 (Si/Al ratio 40 and 100), and Beta zeolites (Si/Al ratio of 150, 19, and 12.5) were purchased from Zeolyst, whereas Beta zeolites (Si/Al ratio of 75 and 15) were provided from Clariant. The water used in all experiments is deionized. All chemicals were used as received without further treatment if not specified.

Catalyst synthesis

Zeolites pre-treatment

Prior to the reaction, the zeolites were calcined in a static air oven, heating profile: i) go to 150°C with a heating rate (HR) of 10°C min⁻¹ for 30 min, then ii) go to 550 °C for 4 h with a heating rate of 2 °C min⁻¹. The oven has been cooled down without any control over the ramp.

Synthesis of Nb₂O₅

The synthesis procedure of layered Nb₂O₅ has been adapted from previously reported work.^{1,2} In a typical synthesis, 25 mL of deionized water containing 0.35g of ammonium oxalate was mixed with 70 mL of niobium oxalate solution (Nb: 0.25 mol L⁻¹). The solution was sealed in a 100 mL autoclave with Teflon liner. The synthesis temperature was kept at 180 °C in an oven without stirring for 24 h. When cooled, the sample was centrifuged and washed with deionized water and dried at 100 °C for 12 h. The obtained solid was calcined at 400 °C (heating rate of 5 °C min⁻¹) for 4 h in static air. The oven has been cooled down without any control over the ramp.

Regeneration of spent zeolite

After the reaction procedure, the spent catalyst was separated from the reaction mixture as described in Catalytic experiment section. The collected catalyst was then placed on a ceramic crucible, and then thermally treated in a static air muffle oven with the following heating profile i) go to 100°C with a HR of 10°C min⁻¹ for 3h to dry from solvent residual, then ii) go to 550 °C for 4 hours with a heating rate of 2°C min⁻¹. The oven has been cooled down without any control over the ramp.

Instrumental methods

Gas chromatography coupled with mass spectrometer (GC-MS) and Flame Ionization Detector (GC-FID)

The qualitative analysis of products has been conducted using a gas chromatography device coupled with a mass-spectrometer (GC-MS) -Agilent 5973 MSD- equipped with (Agilent HP-5MS) column. The chromatographic run has been set with a time of 40 min, and injection volumes of 1.0 μL , and N_2 gas has been used as carrier gas with a total flow of 28.3 mL min^{-1} . The injection has been set in Split mode with a split ratio of 25:1 while the inlet has been kept at 300°C. The temperature program for the column oven has been set as follows: start at 50°C and then increase to 150°C with a heating rate of 10°C min^{-1} . Then the temperature increased to 200°C with a heating rate of 15°C min^{-1} and then up to 300° with a heating rate of 15 min^{-1} . The MS detector has been set to scan between 50 and 500 m/z . The solvent delay has been set at 2.6 min. Noteworthy, Before introducing the samples into the GC-MS, the sample was diluted by a factor of 2 in 4 ml ethyl acetate. The dilution step is necessary to protect the detector's filament from degradation. For the quantitative analysis, gas-chromatography coupled with a flame ionization detector (GC-FID) has been used. The method's settings have been set identically to the GC-MS analysis.

Pyridine adsorption followed by Fourier-transform infrared spectroscopy (Py-IR).

Py-IR was applied to quantify the density of Brønsted acid sites of solid catalyst in a Nicolet 6700 spectrometer (Thermo Fisher Scientific) equipped with a DTGS detector. In a typical measurement, the samples were pelletized into a self-supported wafer (*ca.* 10 mg cm^{-2}) and pretreated at 400 °C under a vacuum (< 0.1 mbar) for 6 hours before measurement. Then, the sample cell was cooled to around 50 °C, and *ca.* 5 mbar of pyridine vapor was introduced to the sample cell until saturation. Upon saturation, the samples were again exposed to vacuum (< 0.1 mbar) to remove the excess of pyridine, and the temperature was increased to 150 °C to start the desorption step (2 hours at 150 °C under < 0.1 mbar vacuum). The spectral acquisition was performed at the different stages of the measurement (before pretreatment, after pretreatment, during and after adsorption, and after the desorption step) with an accumulation of 128 scans at a resolution of 2 cm^{-1} . The amount of Brønsted acid sites was calculated by integrating the band areas of the peaks at 1545 cm^{-1} , respectively and using the corresponding integrated molar extinction coefficient ($\epsilon(\text{B})= 1.67 \text{ cm } \mu\text{mol}^{-1}$), reported in the literature.³

Thermogravimetric analysis (TGA).

TGA was performed under O_2 using a TGA/DSC3+ (thermogravimetric analysis/differential scanning calorimetry 3+) complex (Mettler Toledo). About 15 mg of spent catalyst was heated with the following steps: i) initially, the temperature was heated from room condition to 150°C at a heating rate of 10°C min^{-1} under a N_2 flow of 90 ml min^{-1} for 30 min, ii) the sample was heated to 600°C with the same N_2 atmosphere at 10°C min^{-1} , iii) when the temperature reached the the atmosphere has changed from N_2 to O_2 and kept in an isotherm step for 2h. Switching from N_2 to O_2 atmosphere allows to distinguish from soft and hard coke, as previously reported.^{4,5} Noteworthy, since the catalyst was used in water and still presented a high amount of water the 100% mass for TGA was set as the weight after the first step at 150°C.

Nitrogen physisorption (N₂-physisorption).

N₂-physisorption was conducted at -196 °C using a TriStar 3000 (Micromeritics). The sample (ca. 30 mg) was degassed under an N₂ flow at 300 °C for 6 hours before measurement. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The total volume (V_{pore}) was determined using the adsorption amount at $p/p^0=0.99$. The t -plot method was used to determine the micropore volume (V_{micro}).

Powder X-ray diffraction (XRD)

XRD diffractograms were collected on a high-throughput STOE STADI P Combi diffractometer in the transmission mode with focusing Ge (111) monochromatic X-ray inlet beams ($\lambda = 1.5406 \text{ \AA}$, Cu K α source).

UV-Vis Spectrophotometry

The UV-Vis measurements were carried out on a Varian Cary 5000 UV–Vis–NIR spectrophotometer at room temperature against a halon white reflectance standard in the 5000–40000 cm⁻¹ energy range.

¹H-NMR procedure

Liquid-phase ¹H-NMR spectra were acquired on Bruker Avance 400 MHz instrument. In a typical experiment, 5-30 mg of dried sample was dissolved in 500 μL of a deuterated solvent (CDCl₃ or DMSO-d₆).

Catalytic experiments

O-Demethylation in water using heterogeneous catalyst

The heterogeneously catalyzed O-Demethylation reaction was performed in a 12 mL homemade micro-batch reactor equipped with a barometer for pressure reading and magnetic stirring, as shown in Figure S1. In a typical reaction, 4.6 mL of water was placed inside the reactor as a solvent with 200 mg of catalyst and 2.38 mmol of reactant, corresponding to 400 mg, 451 mg, and 355 when methyl syringol, propyl syringol, and syringol are used as feedstock, respectively. The following heterogeneous catalysts have been used: Nb_2O_5 ; Beta Zeolite (with 5 different Si/Al ratio: 12.5 ; 15; 19; 75; and 150) ; ZSM-5 zeolite (with 2 different Si/Al ratio of 40 and 100) ; MOR zeolite (with Si/Al ratio of 30). Prior to heating, the reactor was flushed three times with N_2 to remove oxygen, and regulated with the aimed value, *i.e.* 1, 10, and 20 bar. The reactor has been heated to the aim temperature - ranging from 190°C to 250°C – by using a round heating plate equipped with an aluminum block to ensure heating transfer. During the heating process and reaction time, the reactor's internal temperature has been controlled by a thermocouple. Similarly, the autogenous pressure was monitored using the barometer. To ensure minimal conversion during the pre-heating process the reactor was placed in the heating block only when the aim temperature was reached. For the same aim, the magnetic stirring was kept off until the feed had reached the aim temperature and then turned on at approximately 750 rpm. The reaction time was taken as 0 min only when the stirring has started. Afterwards, the reaction was kept for the desired time, *i.e.* 0 -15-30-60-120-240-360 min. After the reaction time has been reached, the reaction has been quenched by turning off the stirring, removing the reactor from the block and keeping it at room temperature for approximately 10 minutes and then placed in an ice bath to be further cooled-down.

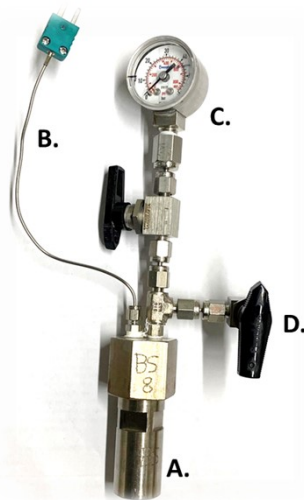


Figure S1: The setup used for the O-demethylation experiment using a heterogeneous catalyst, consisting of a) a stainless steel vessel of 12 mL, b) an inner thermocouple for temperature reading, c) a barometer for pressure reading, and d) a three-way valve for gas purging and degassing.

After the O-demethylation reaction, a three-phases mixture is produced, consisting of a water phase

(solvent), an oil phase (product) and a solid phase (catalyst). Moreover, liquid-liquid extraction method (LLE) using approximately 20 mL of ethyl acetate (EA) as a solvent was applied to extract organic molecules from the aqueous phase. Initially, the reactor vessel and the reactor head were washed with approximately 5 mL of EA. Afterwards, the water-phase, containing the catalyst, has been washed with approximately 5 mL EA, shaken vigorously, and separated by centrifugation (3800 rpm during 4 min with no additional heating). The upper organic phase has been collected with Pasteur pipette. This step has been repeated three times to ensure a complete extraction of organic molecules from the water phase. Moreover, an additional centrifugation step has been conducted to separate the catalyst from the water phase (3800 rpm for 8 min with no additional heating). 150 mg of 2-isopropylphenol has been added to the organic phase as a standard compound and analyzed with gas chromatography equipped with Mass Spectrometry (GC-MS) and Flame Ionization Detection (GC-FID). The water phase was subjected to a High-Performance Liquid Chromatography (HPLC) analysis. All the product quantification procedures are reported below in the dedicated section.

O-Demethylation in water using HCl as a homogeneous catalyst

The homogeneously catalyzed O-Demethylation reaction was performed in a commercial 30 mL Parr autoclave. Initially, a Solution of 0.121 M of HCl was prepared by diluting 0.162 mL of the 37 wt% HCl stock solution with 50 mL of water. In a typical reaction, 12 mL of the 0.121 M HCl solution was placed inside the reactor containing water as a solvent and 1.45 mmol HCl as a catalyst, 2.3 mmol of methyl syringol as a reactant, corresponding to 400 mg. Prior to heating, the reactor was flushed three times with N₂ to remove oxygen, and set to the aimed value of 45 bar N₂. High N₂ pressure is necessary to ensure that HCl is in the liquid phase. The reactor has been heated to the aimed temperature - ranging from 190 to 250°C. After the reaction time has been reached, the reaction has been quenched, firstly, using compressed air for approximately 30 min, until reaching 100°C, and then, placing the reactor vessel in an ice bath to be further cooled down. After the reaction, the sample mixture has been treated analogously to the above-reported heterogeneous O-demethylation procedure.



Figure S2: Commercial 30 mL Parr autoclave used for the HCl-catalyzed O-demethylation.

Product analysis and quantification

The product mixtures from the catalytic experiment (ODM) and the MMC glycidylation have been investigated qualitatively and quantitatively using gas chromatography equipped with mass spectrometer (GC-MS) and flame ionization detector (GC-FID), respectively.

For the MSyr O-demethylation it has been conducted a derivatization step prior to the GC injection, while the MMC glycidylation products (and Mixture I and Mixture II) has been injected without a further derivatization step.

The ODM reaction mixture has been derivatized with (N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA), *i.e.* silylated, to increase the response and minimize product condensation within the GC column. Initially, a portion of approximately 3mL of the organic phase, containing IPP as standard, has been dried with anhydrous MgSO₄. The drying step is necessary to ensure complete derivatization of the phenolic -OH. Later, 90 µL of dried organic phase mixture was added to 85 µL MSTFA, and 670 µL of pyridine, used as a solvent and silylation initiator. The silylation mixture was capped, shaken, and placed in an oven at 80°C for 30 min.

The quantification has been calculated by using the response factor (RF) relative to the IPP standard. The RF has been measured with calibration curves with standard compounds for the following *i*-th molecules: 4-methyl syringol (M-Syr), 4-propyl syringol (4-PS), gallol (Gal), and 4-methyl-methoxy catechol (MMC) compounds. These curves have been done with 4 points in the linear molar range of 0.095-1.357 mmol. The mixtures of standards have been silylated with the same procedure described above for the products. Accordingly, the Response Factor (RF) for the *i*-th compound was determined relative to the IPP as an external standard as follows⁶:

$$RF_i = \frac{A_i}{A_{STD}} \cdot \frac{N_{STD}}{N_i}$$

Where N is the known number of moles and A is the FID-measured area.

The RF of the following compounds has been calculated using the effective carbon number (ECN) methods⁷⁻⁹: 4-methyl gallol (M-Gal), 4-propyl gallol (P-Gal), 4-propyl methoxy catechol (P-MC), mono-glycidylated MMC (G-MMC), di-glycidylated MMC (GG-MMC), dioxirane-MMC (DX-MMC), di-hydrochlorinated MMC (HH-MMC), mono-hydrochlorinated– mono glycidylated MMC (GH-MMC), and bis-MMC. The Response Factors (RF) are determined as follows:

$$RF_i = \frac{ECN_i}{ECN_{STD}}$$

Where Herein i is referred as Methyl-pyrogallol and Syringol, ECNi refers to the effective carbon number of molecule i and ECN_{STD} refers to the effective carbon number of the internal standard (IPP) that has been used.

The ECN has been calculated using the values from literature as follows in **Table S1**¹⁰:

Table S1. ECN values used for calculation, calculated from ref¹⁰

Functional group	Condensed formula	ECN used
Silyl-	C-O-Si(CH ₃) ₃	3.69
Methoxy	-O-CH ₃	0
Glycidyl-	OCH ₂ CH(O)CH ₂	2
Aliphatic/Aromatic	C-	1
Ether	C-O-C	-1
Primary alcohol	-C-OH	-0.5
Hydroxyl-dioxirane	-OCH ₂ CH (CH ₂ OH) O	1.5
Hydrochlorin-	-CH(OH)CH ₂ Cl	1.38

The overall ECN has been calculated by the sum of the ECN of all the groups presented in the molecule.

The product conversion (X), yield (Y), and selectivity (S) expressed in mol% have been calculated as follow:

$$X_i = 1 - \frac{N_j}{N_j} \cdot 100$$

$$Y_i = \frac{N_i}{N_j} \cdot 100$$

$$S_i = \frac{Y_i}{X_j} \cdot 100$$

Where N_i stands for the number of moles of the i -th substances and N_j the moles of reactant left in solution. Those numbers have been calculated from the FID integration as follows:

$$N_i = \frac{A_i}{A_{STD}} \cdot N_{STD} \cdot RF_i$$

where A_i stands for the Peak area from (FID) of the silylated i -th compounds, A_{STD} for the peak area of Silylated IPP from FID, n_{STD} for the known number of moles of IPP and RF_i for the response factor for the i -th compounds.

The turn-over frequency (TOF) is expressed in h^{-1} and has been calculated from the initial rate r_i as follows

$$TOF = \frac{r_i}{n_{BAS}}$$

where n_{as} is the number of active acidic sites, i.e. the Brønsted calculated from Table S1, and r_i is the initial rate corresponding to the slope of the regression line of the produced MMC mol Δn_{MMC}^t during the first three-time points (0, 15, and 30 min). Where Δn_{MMC}^t is calculated as follows:

$$\Delta n_{MMC}^t = n_{MMC}^t - n_{MMC}^0$$

where t indicates the mol produced at the given time, i.e. 0, 15, and 30 min, and n_{MMC}^0 the MMC mole at the 0 time. Please note that for definition Δn_{MMC}^0 is equal to 0.

Liquid-phase Isothermal experiments

Liquid-phase adsorption isotherm of MMC, MSyr, and MGal on catalysts was obtained by immersing 10-250 mg of Beta 75 zeolite in an aqueous solution containing the molecules at a defined concentration at 25°C for 36 h to ensure saturation of the adsorption. After the adsorption, the zeolites were separated from the solution, dried in air at room temperature for 48 h, and analyzed with UV-Vis spectrometer.

Synthesis of epoxy thermoset

MMC O-glycidylation and isolation

To synthesize the di-epoxy monomer, GG-MMS a O-glycidylation procedure has been adapted from existing literature.^{11,12} The protocol employs an excess of epichlorohydrin as a reactant benzyltriethylammonium bromide (TEBAC) as a phase transfer catalyst (PTC). Herein, 9.74 mmol, corresponding to 3 g of MMC was placed in a 50 ml glass round flask with an excess epichlorohydrin (MMC: epichlorohydrin molar ratio 1:20), corresponding of 15 g. Then 70 mg (1.95 mmol) of TEBAC was added (MMC: TEBAC molar ratio 10:2) as a phase transfer catalyst (PTC). The flask was flushed with N₂ to displace O₂, creating an inert atmosphere. During the reaction, the flask was closed with a septum and a N₂ balloon was connected through a needle to create a slight N₂ overpressure preventing O₂ from penetrating. The reaction mixture was heated at 80°C for 5 h with an oil bath while stirring.

After 5h, the flask was removed from the oil bath and kept cooling at room temperature. Therein, 2 mL of 40% NaOH solution was added dropwise to the reaction mixture(OH⁻ : MMC molar ratio 4:1), in order to facilitate the epoxide ring closing as well as to neutralize any possible acidic functionalities. The reaction was kept at room temperature for additional 3 h while stirring.

After the reaction, Dichloromethane (DCM):H₂O liquid-liquid extraction procedure was conducted to separate the products. The extraction was repeated threefold, with fresh DCM and water introduced at every iteration.

The organic phase containing the products was then dried with approximately 3 g of anhydrous MgSO₄ followed by filtration with a paper filter (pore size of 120 μm).

Finally, the DCM and the excess on un-reacted epichlorohydrin have been removed with rotary evaporation (oil bath temperature 56°C, rotation 120 rpm.). A vacuum pressure of 750 mbar was applied for 10 minutes and gradually reduced to 9 mbar to completely dry the product mixture. The obtained oily-mixture has been noted as G-MMC-Mix

In order to isolate GG-MMC, silica column chromatography has been used with acetone and ethyl acetate as solvents. The fractions have been collected in 100 ml test-tubes, and the products have been identified with ¹H-NMR and GC-MS and quantified with GC-FID. In the case of GC, the products mixtures have been injected without any further derivatization step.

Glycidyl concentration (G_{eq}) in mixture

For the G-Mix epoxy resin the glycidyl concentration in the mixture was measured using ¹H-NMR. Initially, 5 mg of vanillin was added as reference STD to 15 mg of G-mix resins and solubilized in 500 μL of CDCl₃ and analyzed with ¹H-NMR. Then, the vanillin aldehydic proton has been used as reference with an integration value of 1. Then the G_{eq} has been calculated as follow:

$$G_{eq} = \sum_i I_{CH-G} / M_{mix} * N_v \quad [mol_{epoxy} g_{mix}^{-1}]$$

Where the $I_{\text{CH-G}}$ stands for the $^1\text{H-NMR}$ integration of C_2 proton of the glycidyl- group (typically in chemical shift 2.80-3 ppm); M_{mix} stands for the mass of mix used in the calculation, and N_v is the number of vanillin mole used as a standard. Please note that the integration of the vanillin aldehydic is omitted as it is unitary.

Curing of produced thermoset.

To prepare rectangular cured epoxy resins (9 x 12 x 1 mm), 200 mg of epoxy-resins was combined with stoichiometric amount of isophorone diamine (IPDA) (molar ratio of NH_2 : epoxy 1:2). The mixture was mixed extremely gently, to prevent the formation of air bubbles. To remove solubilized air, preventing bubbles formation, the air was removed in vacuo. Afterward, the mixture was poured into a silicon mold (Smooth-Sil 950) and cured in a static air oven with a 3-segment heating profile consisting of i) 80°C for 1h, followed by ii) 110°C for 1h, and iii) 130°C for 1 h. Afterward, the sample was removed from the oven and allowed to cool at room temperature for 3 hours then the produced epoxy-thermoset was removed from the mold. Afterward, the prepared polymer bars were analysed using Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC), and thermogravimetric analysis (TGA).

Characterization of MMC-based epoxy thermoset

Dynamic Mechanical Analysis (DMA)

The epoxy thermoset(s) have been characterized by Dynamic Mechanical Analysis (DMA) using a DMA Q800 instrument from TA Instruments with a single cantilever clamp. The temperature program consisted of a heating ramp between 20 and 200°C at 2°C min⁻¹ (20 μm amplitude, 1 Hz frequency). The glass transition temperature was defined as the maximum tan (δ) temperature. The data acquired were processed with TA Universal Analysis.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was performed using a DSC Q200 instrument from TA Instruments. The temperature program consisted of two heating-cooling cycles between 20 and 180°C, with a heating/cooling ramp of 10°C min⁻¹ under N₂ atmosphere. Samples of 5-8 mg were accurately weighed in aluminum pans and covered with an aluminum lid. The glass transition temperature was defined as a step change in the heat flow during the second heating cycle. The data acquired were processed with TA Universal Analysis.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a TGA 2 instrument from Mettler Toledo with autosampler. A portion of the sample was weighted on a precision scale (typically 10 to 20 mg) and heated in the TGA machine. To discriminate between physisorbed molecules, soft and hard coke contributions we adapted a methodology reported in the literature.^{4,5} Accordingly, the spent catalyst was heated with the following steps: i) initially the temperature was heated from room condition to 150°C at a heating rate of 10°C min⁻¹ under a N₂ flow of 90 ml min⁻¹ for 30 min ii) the sample was heated to 600°C with the same N₂ at 10°C min, iii) at 600°C the atmosphere has changed from N₂ to O₂ and kept in an isotherm step for 2h.

Supporting Tables, and Figures

Table S2. Literature overview for the homogeneously catalyzed ODM

Feedstock	Product	Product Yield (mol%)	Catalyst used	Temperature (°C)	Reaction time (h)	Ref
Syringol	Pyrogallol	82	LiBr / Hbr 53:6 wt	100	2	13
Synapyl alcohol	Pyrogallol	99	H ₂ SO ₄	250	1	14
Syringol	Pyrogallol	99	Ru-Co, Lil, and triphos ligand	190	10	15
Dihydrosinapyl alcohol	Propyl-gallol	-	HCl	250	-	16
Propyl syringol	Propyl gallol	98	LiBr and HCl	110	2	17

Table S3. Textural properties and acidity of catalysts

Material	Si/Al ^a (mol mol ⁻¹)	S _{BET} ^b (m ² g ⁻¹)	V _{total} ^b (cm ³ g ⁻¹)	V _{micro} ^b (cm ³ g ⁻¹)	B ^c (μmol g ⁻¹)
Beta 12.5	12.5	515.8	0.90	0.17	238
Beta 15	15	584.3	0.37	0.21	183
Beta 19	19	553.7	0.33	0.22	215
Beta 75	75	591.7	0.56	0.21	68
Beta 150	150	546.0	0.46	0.18	26
ZSM-5 40	40	389.4	0.21	0.12	163
ZSM-5 100	100	403.0	0.24	0.11	37
Nb ₂ O ₅	n.a.	171.0	0.32	-	46
Spent-Beta 75	n.a.	409.8	0.47	0.16	-

a Nominal value from provider; **b** measured via N₂ physisorption; **c** measured by Pyridine FTIR. B: Brønsted acid sites.

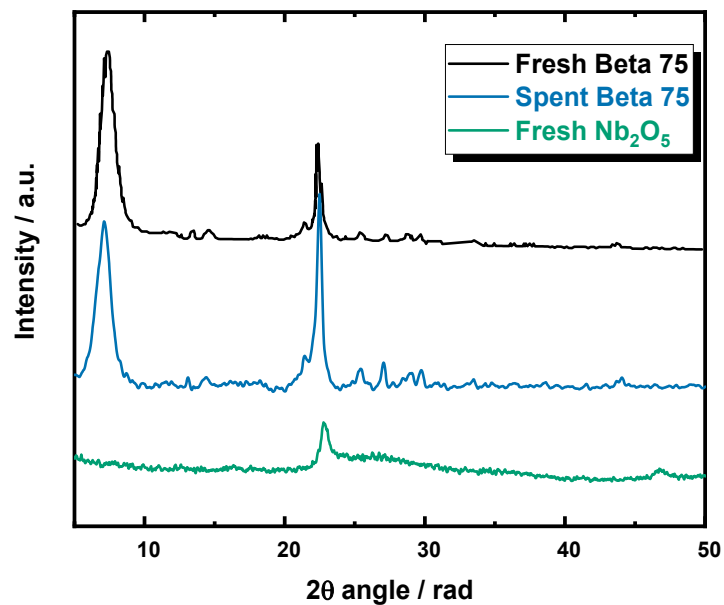


Figure S3. The XRD patterns of Beta 75 (fresh and spent) and fresh Nb₂O₅.

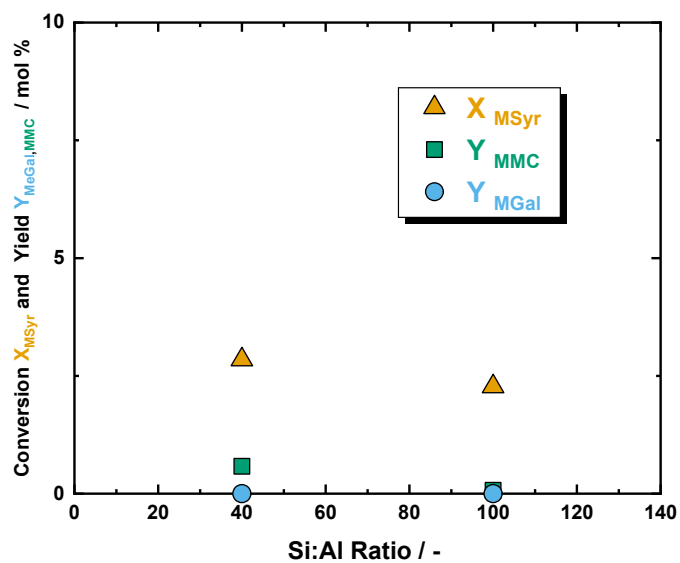


Figure S4: Conversion of MSyr (X_{MSyrr}) and yield of MMC and M-Gal yield (Y_{MMC} and Y_{MGal}) using ZSM-5 catalyst with varied Si/Al ratios. Reaction conditions: Temperature: 210°C, time: 4 h, N₂ pressure= 1 bar, catalyst amount: 200 mg, Si/Al ratio = 40 and 100.

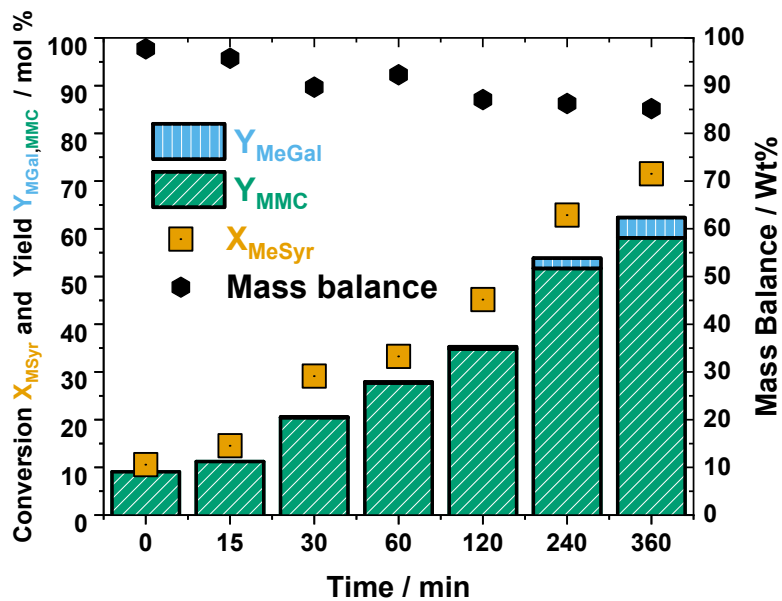


Figure S5: Conversion of **MSyr**, yield of **MMC** and **MGal**, and overall mass balance over Beta 75 as a function of time. Reaction conditions: time: 0min, 15 min, 30 min, 60 min, 120 min, 240 min, 360 min , N_2 pressure 1 bar, catalyst amount: 200 mg, temperature: 210°C.

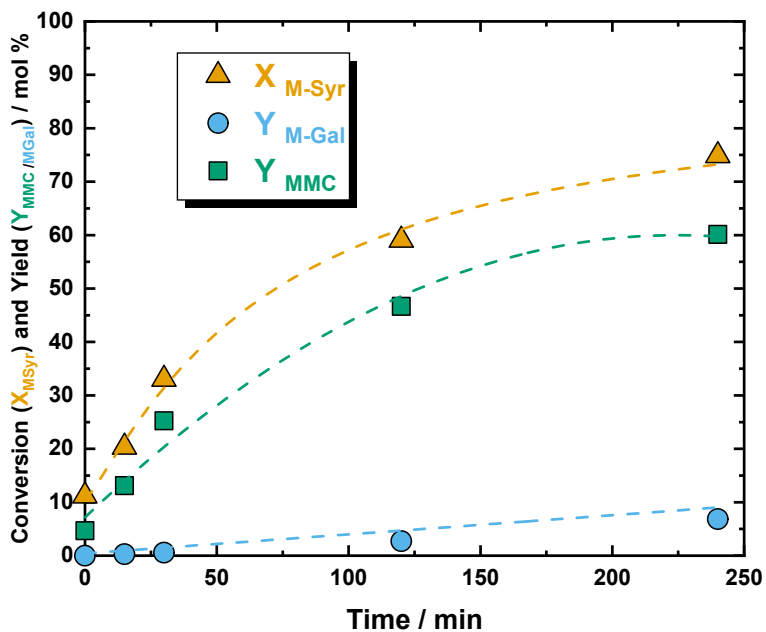


Figure S6: Conversion of **MSyr** and yield of **MMC** and **MGal** over Beta 19 as a function of time. Reaction conditions: time: 0min, 15 min, 30 min, 60 min, 120 min, and 240 min, N_2 pressure 1 bar, catalyst amount: 200 mg, temperature: 210°C.

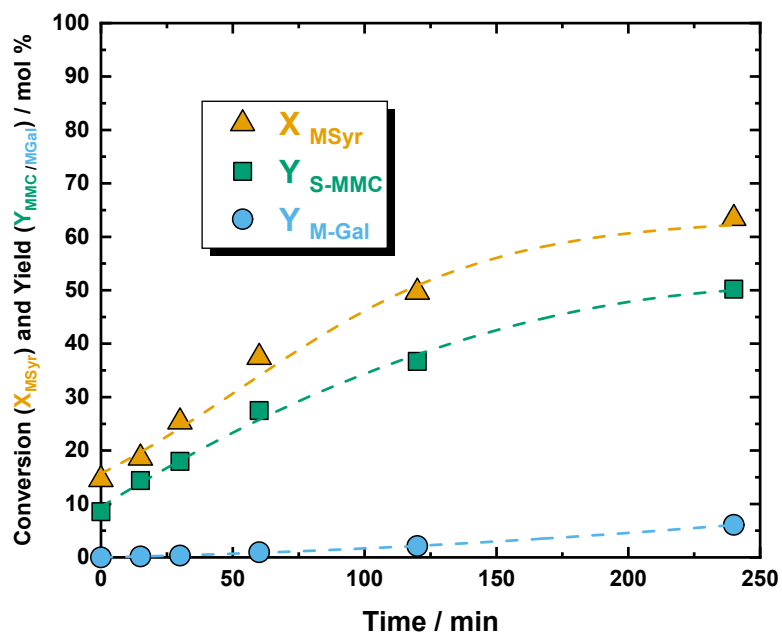


Figure S7: Conversion of **MSyr** and selectivity of **MMC** and **MGal** over Beta 15 as a function of time. Reaction conditions: time: 0min, 15 min, 30 min, 60 min, 120 min, 240 min, 360 min , N₂ pressure 1 bar, catalyst amount: 200 mg, temperature: 210°C.

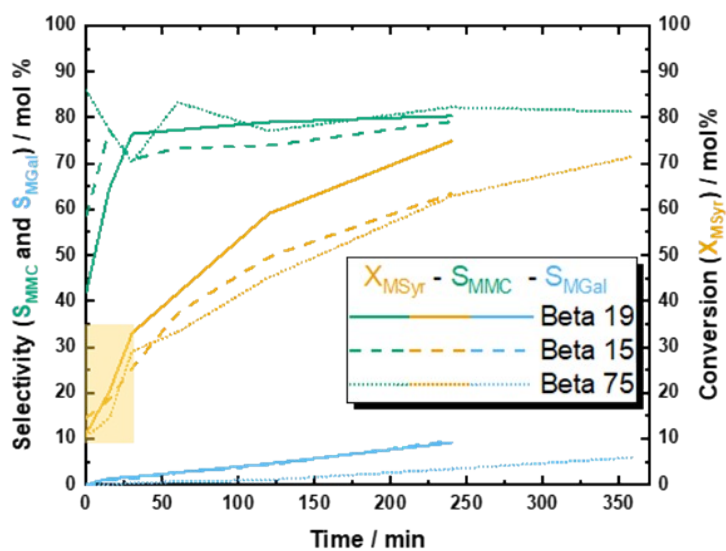


Figure S8: Conversion of **MSyr** and selectivity of **MMC** and **MGal** over Beta 75, Beta 15, and Beta 19 as a function of time. This figure gathers a summary of the data from **Figure 4**, **Figure S4**, and **Figure S5**.

Reaction conditions: time: 0 min, 15 min, 30 min, 60 min, 120 min, 240 min, 360 min, N₂ pressure 1 bar, catalyst amount: 200 mg, temperature: 210°C. The area highlighted in yellow has been used to calculate TOF.

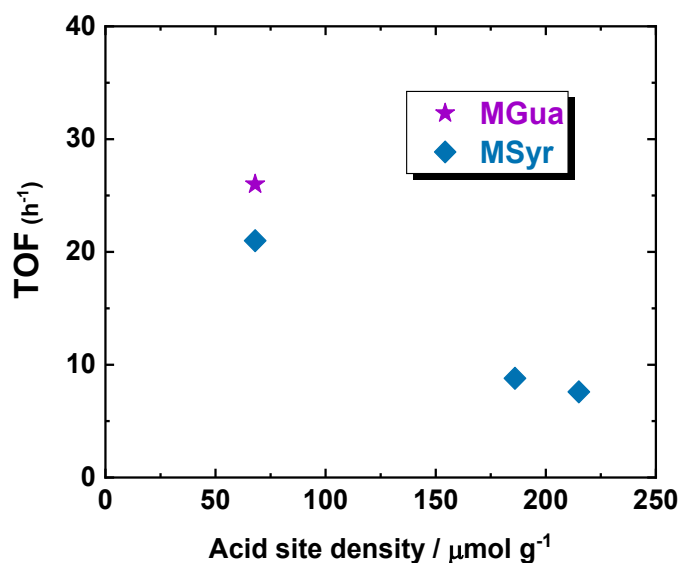


Figure S9: Turn over frequency (TOF) for the production of MMC from MSyr over zeolites with different Brønsted acid sites density (blue prisms) compared with TOF for similar reaction using 4-methyl guaiacol (MGua) from previously published work.¹⁸

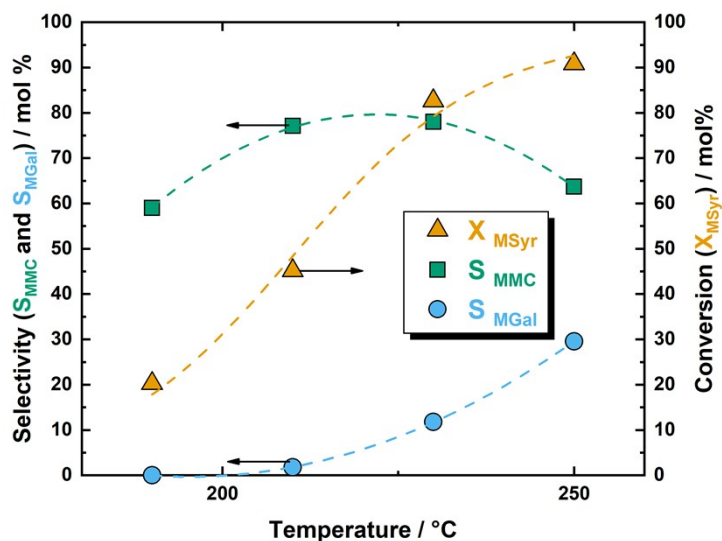


Figure S10: Conversion of MSyr and yield of MMC and MGal over Beta 75 as a function of Temperature. Reaction conditions: time: 2 h, N₂ pressure 1 bar, catalyst amount: 200 mg, temperature: 190°C, 210°C, 230°C, and 250°C.

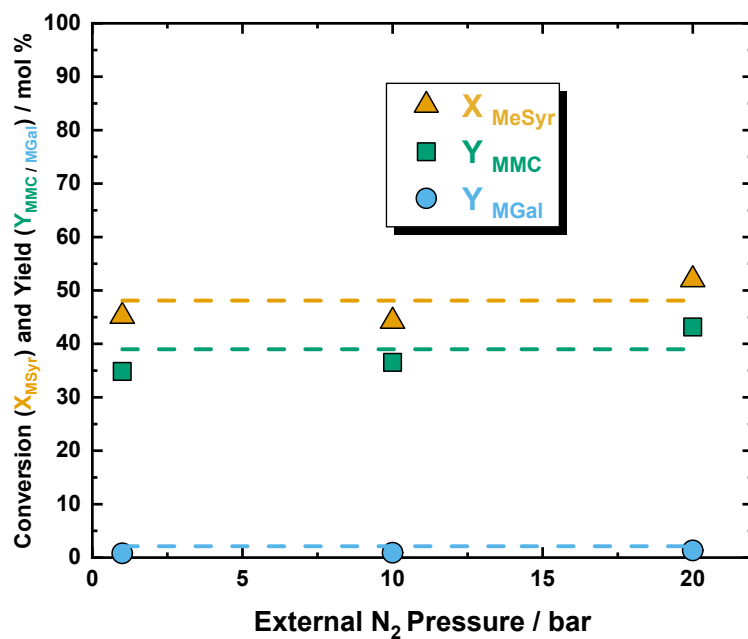


Figure S11: Conversion of **MSyr** and yield of **MMC** and **MGal** over Beta 75 as a function of external N₂ pressure. Reaction conditions: time: 2 h, N₂ pressure 1 bar; 10 bar; 20 bar, catalyst amount: 200 mg, temperature: 210°C.

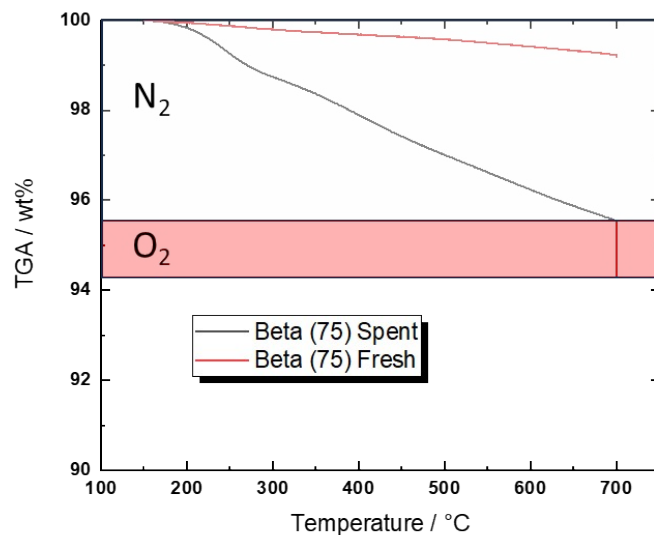


Figure S12: TGA of the fresh Beta 75 as well as the spent catalyst with N₂ atmosphere and with the addition of O₂ at the end of the run (red area).

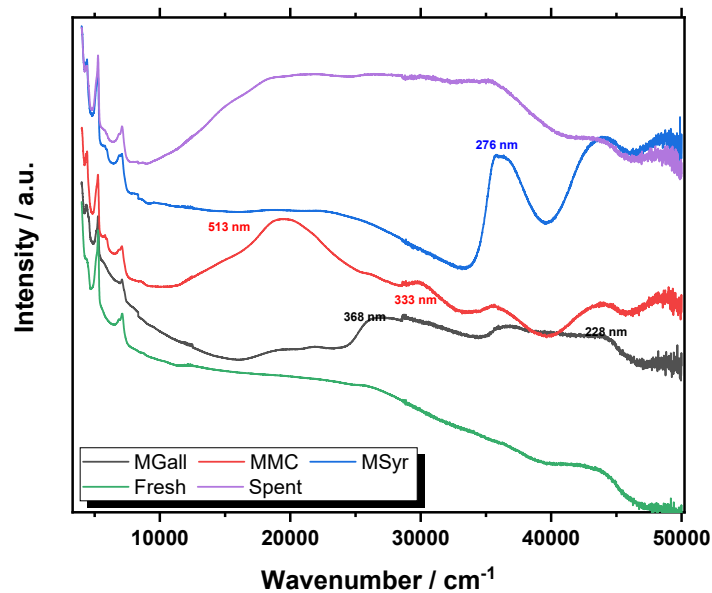


Figure S13: UV-Vis adsorption spectra of the Fresh and spent Beta 75 zeolite, as well as of beta zeolite after the isotherm adsorption experiment with MMC, MSyr, and MGal.

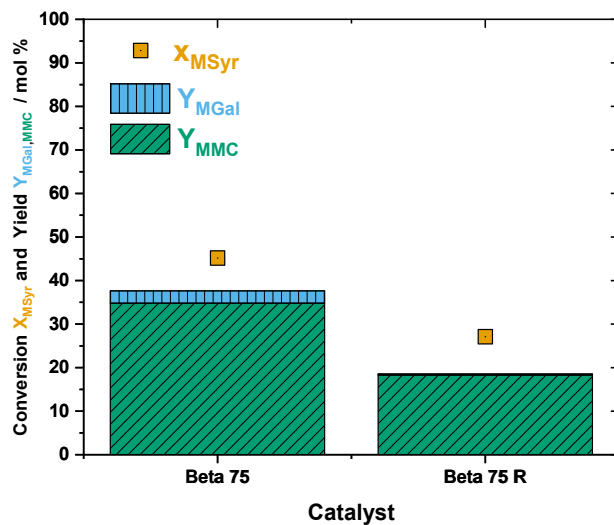


Figure S14: Conversion of MSyr and yield of MMC and MGal over fresh Beta 75 and regenerated Beta 75 catalyst (Beta 75 R). Reaction conditions: time: 120 min, N_2 pressure 1 bar, catalyst amount: 200 mg, temperature: 210°C.

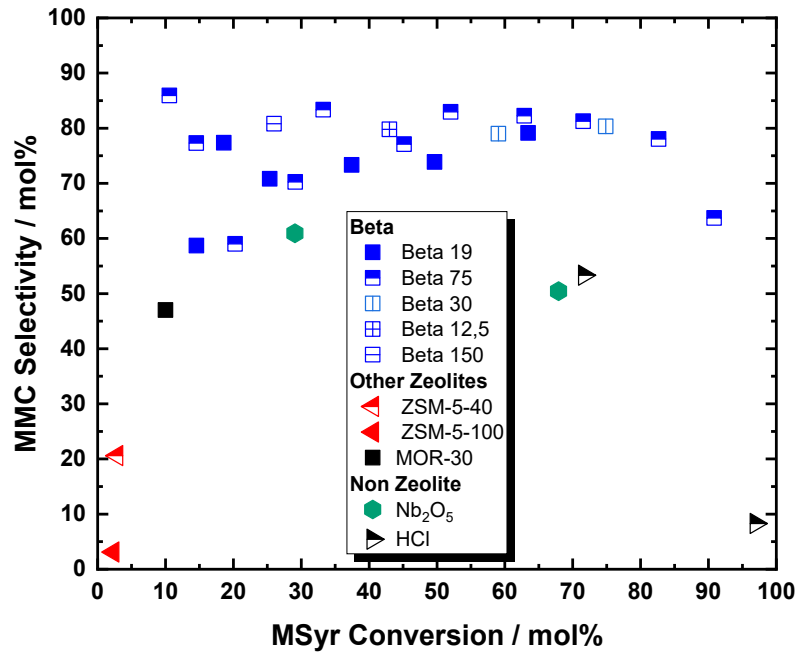


Figure S15: MMC Selectivity as a function of and MSyr conversion. This plot summarizes all the data collected in these studies.

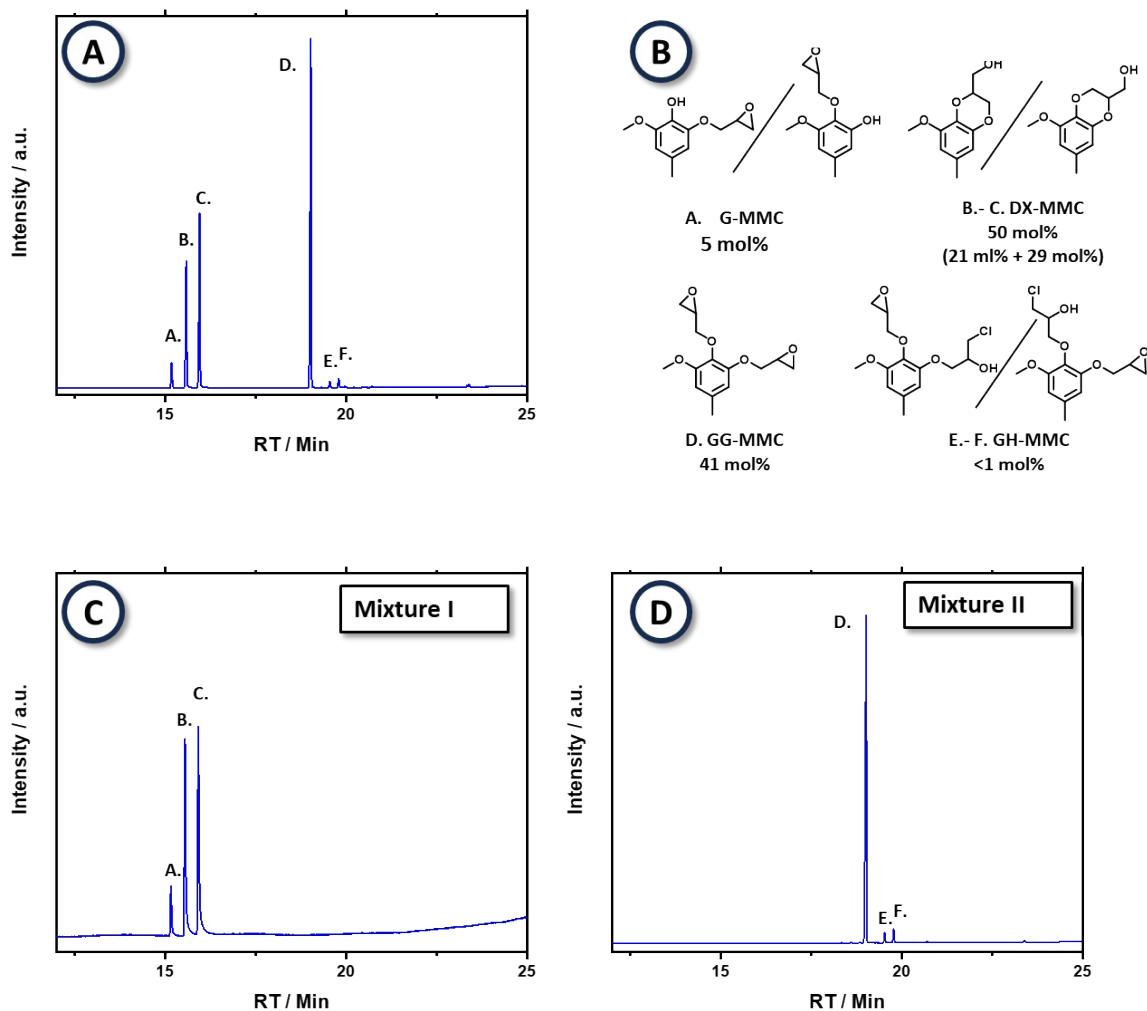
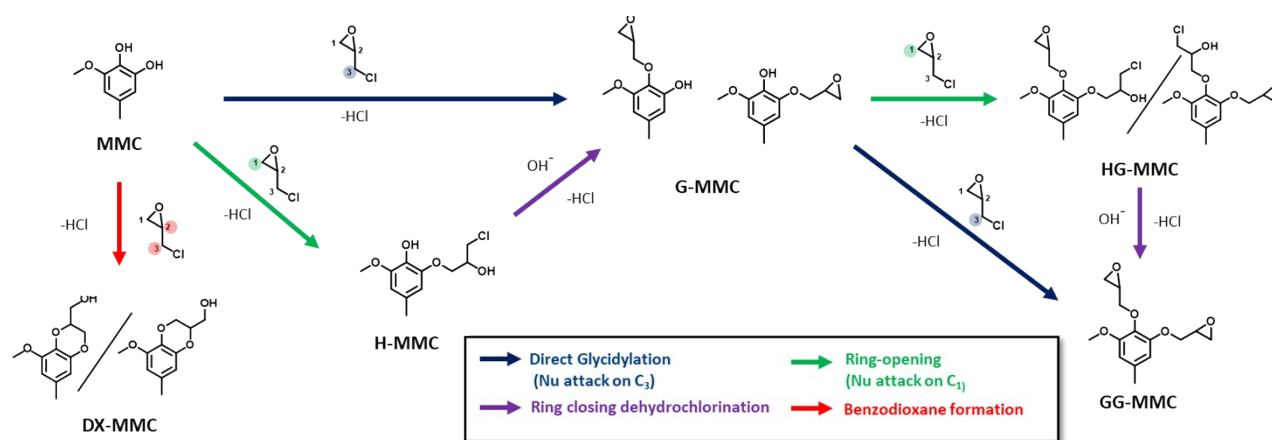


Figure S16: **A)** GC-FID chromatogram of the G-MMC products mixture after glycidylation reaction; **B)** Structure of the compounds identified with GC-MS; **C)** GC-FID chromatogram of the separated mixture I, **D)** Structure of the separated mixture II noted as GG-MMC. Please note that the products have been injected without any derivatization procedure. The fragmentation spectra of the compounds A-F are reported in figure S17-S20 below.



Scheme S1: Proposed reaction scheme for the MMC reaction with epichlorohydrin to form DX-MMC, H-MMC, G-MMC, HG-MMC, and GG-MMC. Blu arrow: direct glycidylation with Nu epichlorohydrine C₃; green arrow: ring opening Nu attack on epichlorohydrine C₁; violet arrow: ring closing dehydrochlorination to form oxirane ring; red arrow: benzodioxane formation.

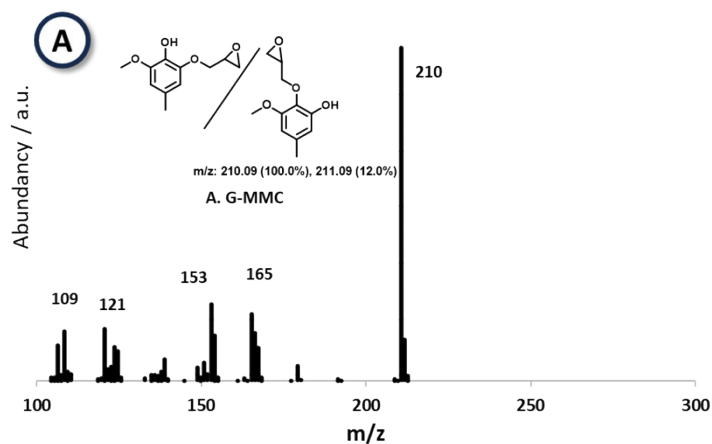


Figure S17: Fragmentation spectra measured with MS detector of the peak A) reported in the chromatogram in **Figure S16**

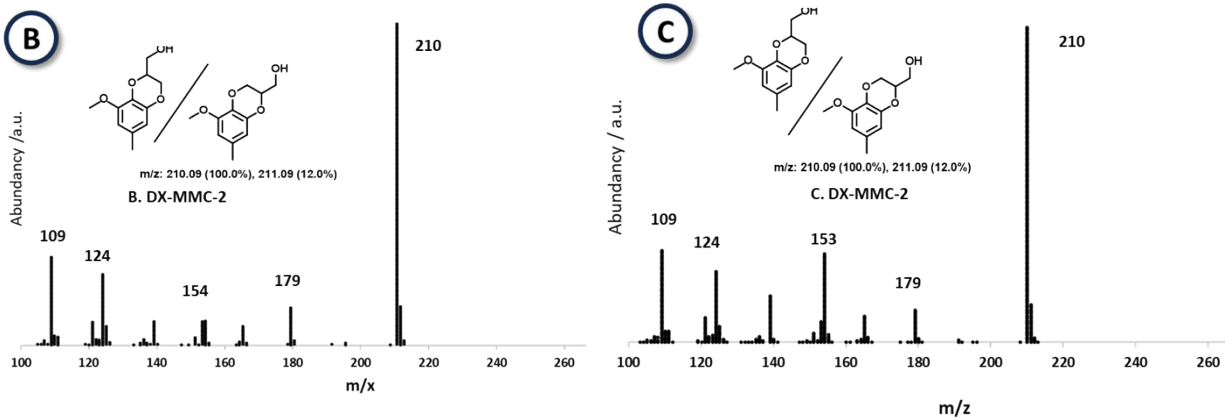


Figure S18: Fragmentation spectra measured with MS detector of the peaks B) and C) reported in the chromatogram in **Figure S16**

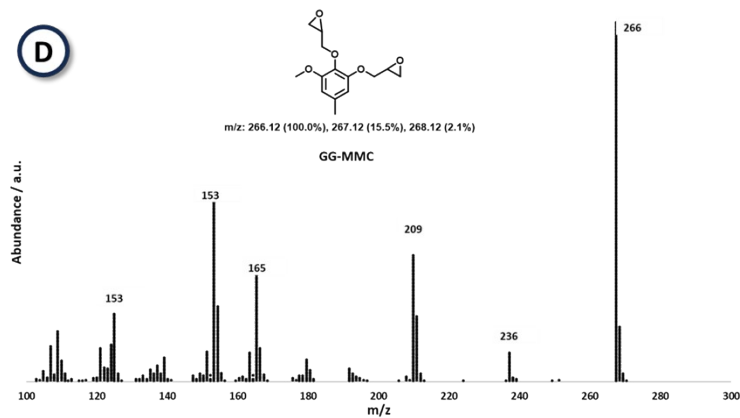


Figure S19: Fragmentation spectra measured with MS detector of the peak D) reported in the chromatogram in **Figure S16**

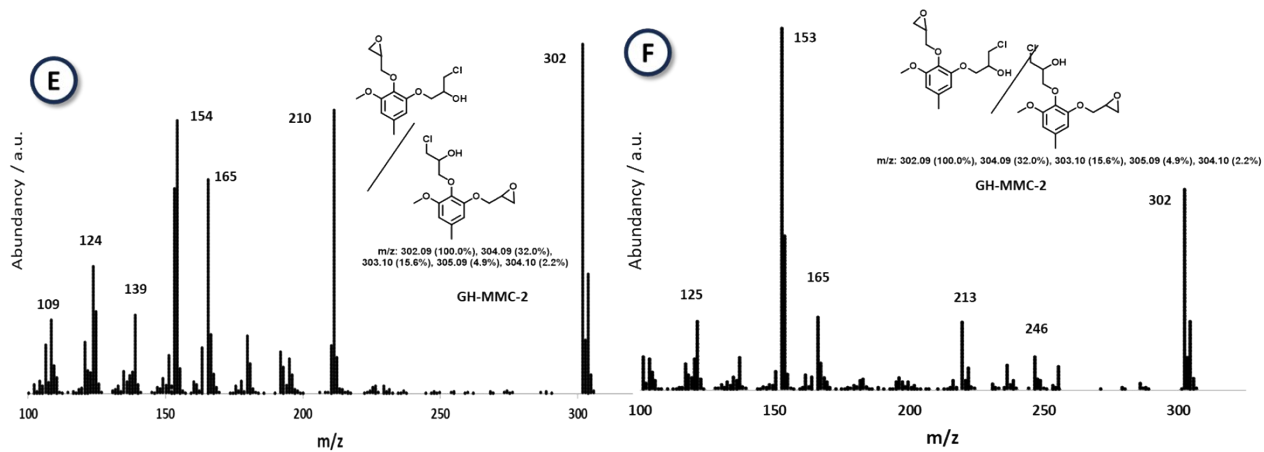


Figure S20: Fragmentation spectra measured with MS detector of the peaks E) and F) reported in the chromatogram in **Figure S16**

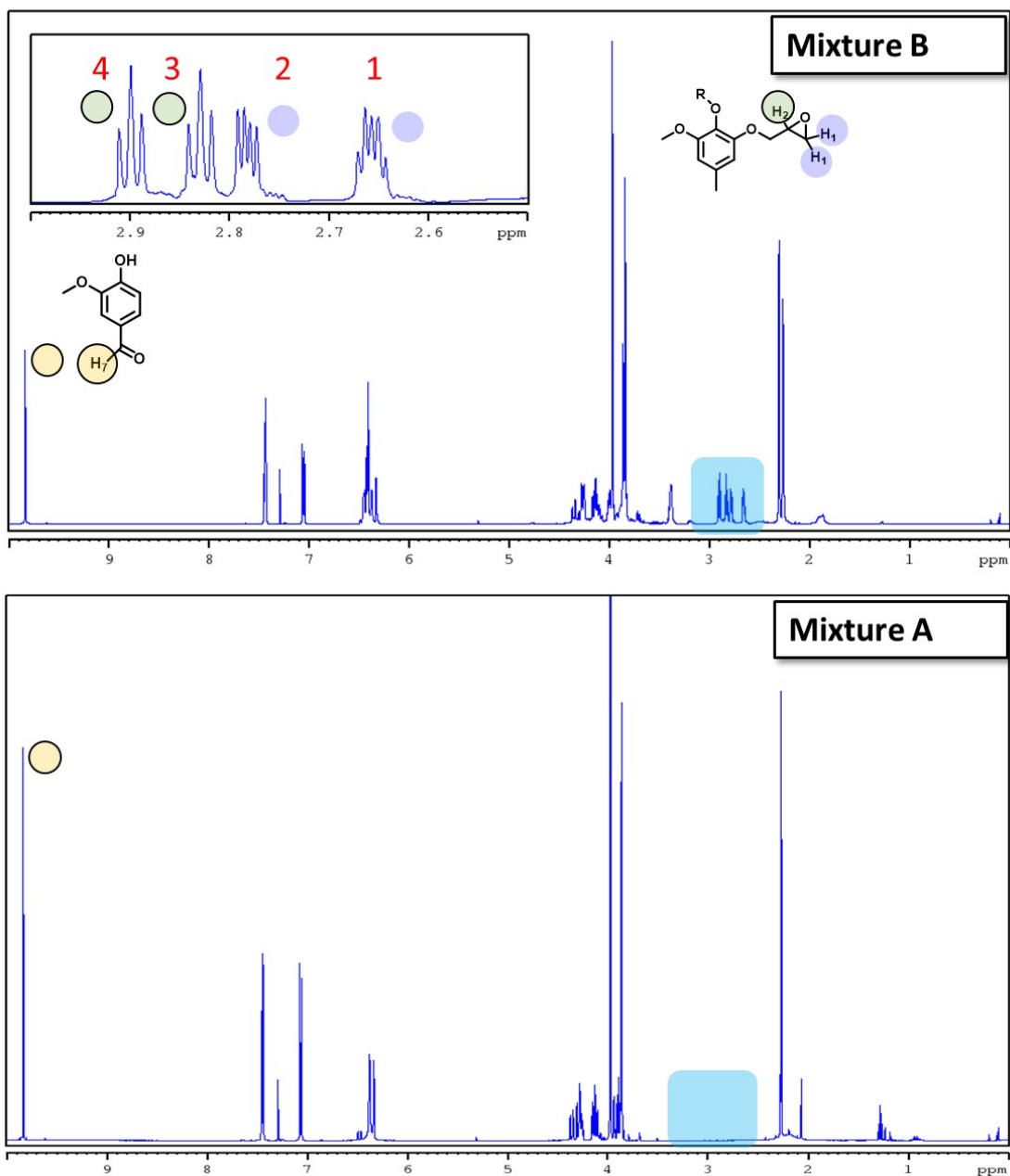


Figure S21: ¹H-NMR spectra of **top)** the purified mixture II used for poly-IPDA-MMC resin and **and, bottom)** the mixture I not glycidylated. In blue is highlighted the proton region used for calculating the epoxy-equivalent and in yellow is reported the aldehydic carbon of syringaldehyde used as standard.

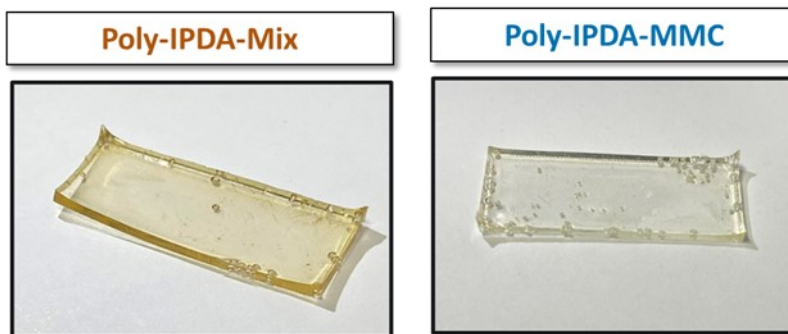


Figure S22: Appearance of the synthesized polymer, **left)** the poly IPDA Mix and **right)** the poly-IPDA MMC. Please note that some air bubbles are formed during the curing.

Table S4. Polymer bars characterization results

Amine-Epoxy Resin	T _g ^a (°C)	T _g ^b (°C)	T _{d5%} ^c (°C)	T _{d10%} ^c (°C)	T _{d50%} ^c (°C)	T _{dmax%} ^c (°C)	CY (%)
Poly-IPDA-MMC	119	126	293 (319)	322 (328)	348 (351)	339 (349)	0 (7)
Poly-IPDA-MIX	55	-	217 (211)	244 (237)	330 (331)	339 (345)	0 (4)

a measured with DSC; b measured via DMA; c measured with TGA in Air, and in brackets in N₂.

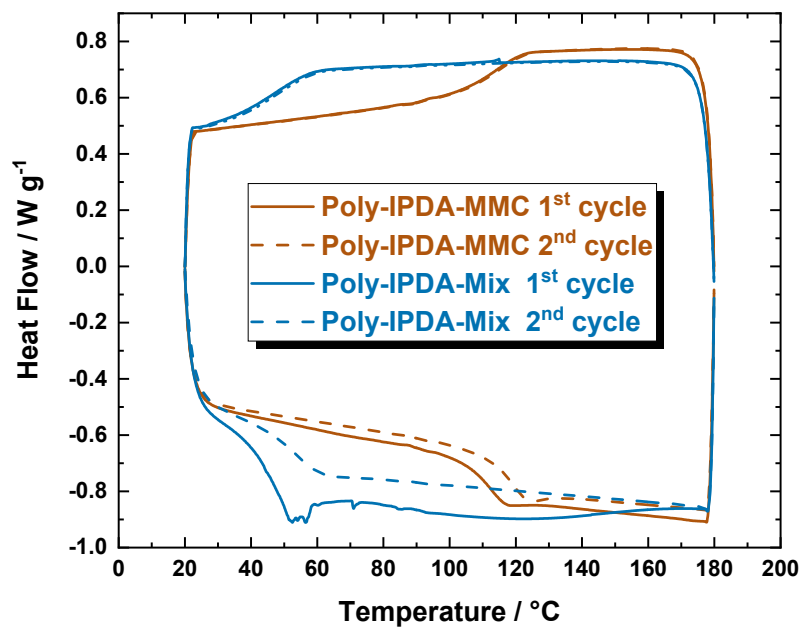


Figure S23: Cyclic DSC of 2 cycles between 20°C and 180°C of the two distinct synthesized polymers, Poly-IPDA-MMC (brown) and Poly-IPDA-Mix (blue).

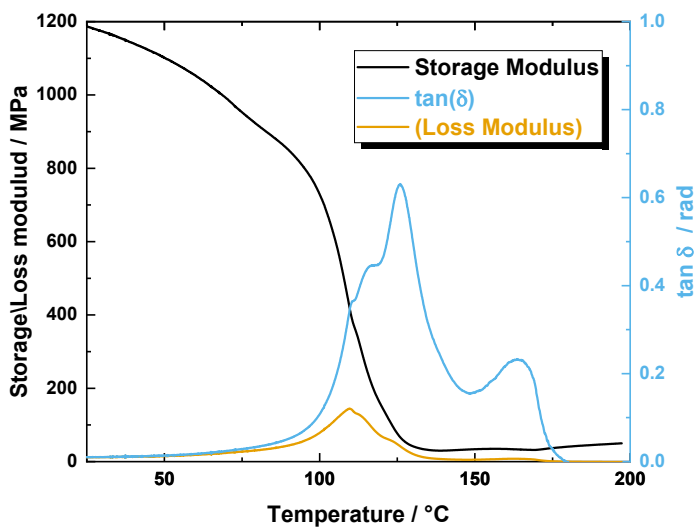


Figure S24: DMA analysis of the poly-IPDA-MMC resins, showing (left) the storage and loss modulus as well as the tan (δ) as a function of temperature.

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