Supplementary Information

Optimized preparation and regeneration of MFI type base catalysts for D-glucose isomerization in water

A. Materials used

For catalyst preparations, the following chemicals were purchased from commercial suppliers and used as received: sodium hydroxide pellets (Laborspirit Lda, P.A.), potassium hydroxide pellets (Ceamed Lda, P.A.), calcium acetylacetonate ($Ca(acac)_2$, TCI, > 98 %), magnesium acetylacetonate ($Mg(acac)_2$, Aldrich, 98 %), magnesium nitrate hexahydrate (Alfa Aesar, 98 %) and sodium nitrate (Panreac, ACS, ISO). Zeolite CBV 3024 (Si/Al = 15) from Zeolyst was calcined at 550 °C (1 °C min^{-1}) for 5 h giving ZSM-5, which was used for preparing the modified materials. For comparative studies, the precursors $Mg(acac)_2$ and $Ca(acac)_2$ were calcined at 550 and 800 °C, respectively, to give the materials denoted as bulk CaO or MgO. For catalytic experiments and chromatographic analyses, the following chemicals were purchased from commercial suppliers and used as received: D-(+)-glucose (Sigma-Aldrich, > 99 %), D(-)-fructose (> 99 %) and acetonitrile (Honeywell, HPLC gradient grade). Deionised water for catalytic tests was degassed under N_2 at 100 °C for 30 min, prior to use. Deuterated water was used for ^{13}C and ^{1}H NMR spectroscopic characterisation of the liquid phase after catalytic runs.

B. Preparation and characterization of the materials

Table S1 indicates the preparation steps carried out per material.

Table S1. Different treatments used to prepare the catalysts from commercial ZSM-5.

Sample	**Desilication of ZSM-5 using NaOH or KOH**			**Impregnation with Mg or Ca (Me) precursor**			
	NaOH	**KOH**	**x (mol mL^{-1})** [a]	**SSI-Mg**	**SSI-Ca**	**IWI-Mg**	**wt% Me**[b]
0.2Na-DZSM5	√		0.2				-
0.4Na-DZSM5	√		0.4				-
0.6Na-DZSM5	√		0.6				-
0.8Na-DZSM5	√		0.8				-
0.2K-DZSM5		√	0.2				-
0.4K-DZSM5		√	0.4				-
0.6K-DZSM5		√	0.6				-
MgNa-DZSM5	√		0.4	√			2.5
5MgNa-DZSM5	√		0.4	√			5.0
MgNa-DZSM5-IWI	√		0.4			√	2.5
5MgNa-DZSM5-IWI	√		0.4			√	5.0
CaNa-DZSM5	√		0.4		√		2.5
Na-ZSM-5[c]	-						-
MgNa-ZSM-5	-			√			2.5

[a] Molar concentration of NaOH or KOH. [b] wt% of Ca or Mg added to the respective precursor material 0.4M-DZSM5. [c] Not subjected to desilication (prepared via ion-exchange of ZSM-5 with NaNO$_3$).

Characterization techniques

Powder X-ray diffraction (PXRD) data were collected on a PANalytical Empyrean diffractometer in a Bragg–Brentano geometry, operating at 45 kV and 40 mA, using Ni-filtered Cu-K$\alpha_{1,2}$ X-radiation (λ_1 =1.540598 Å; λ_2= 1,544426 Å) and a PIXcel 1D detector set at 240 mm from the sample, which was mounted on a spinning flat plate holder. The intensity of the diffracted beam was collected in continuous mode in the range 3.5 to 67.83º (2θ) with steps of 0.026º. A PIXEL linear detector with an active area of 1.7462º was used with a counting time of 70 s per step. For low angle measurements, 0.5095-5º (2θ), PXRD data were collected in the transmission mode and with each sample deposited between *Mylar* foils. The samples were step-scanned in 0.01313º (2θ) steps with a counting time of 120 s per linear detector active area of 2.0º.

The crystalline phases of the bulk metal oxides were identified using POWD-12++ software. The ***relative crystallinity (RC)*** was calculated as the ratio of the total area of the diffraction peaks in the range of ca. 5-10º and 20-30º (2θ) of the modified material relative to the parent commercial zeolite ZSM-5.

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) (for quantification of the elemental atomic ratios, along with the corresponding elemental (Mg, Ca, Na, K, Al and Si) mapping images) were obtained on a Hitachi SU-70 SEM microscope equipped with a Bruker Quantax 400 detector operating at 15 KV. Samples were prepared by deposition on aluminium sample holders followed by carbon coating using an Emitech K 950 carbon evaporator.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed at the Central Analysis Laboratory (University of Aveiro). The measurements were carried out on a Horiba Jobin Yvon Model Activa M spectrometer (detection limit of ca. 20 μg L^{-1} with an experimental range of error of ca. 10%). Prior to analyses, the solids (10 mg) were digested using 1 mL of 28.7 M HF and 1 mL of 12 M HNO_3 and heated at 180 ºC (5 ºC min^{-1}) for 5 min, under microwave irradiation.

Nitrogen sorption isotherms of the modified materials were measured at -196 ºC using a Micromeritics GeminiV 2380; prior to analysis, the samples were degassed at 250 ºC overnight. The specific surface area (S_{BET}) was calculated using the Brunauer Emmett Teller (BET) equation, the total pore volume (V_p) was determined using the Gurvitsch rule (based on adsorption capacity at relative pressure (p/p_0) of *ca.* 0.98), mesoporous and/or external surface area (S_{meso}) and the microporous volume (V_{micro}) were calculated using the *t*-plot method (Harkins and Jura). The mesopore size distribution curves (MSD) were calculated from the adsorption branch, using the BJH method.

^{27}Al magic angle spinning (MAS) NMR spectra were recorded at 182.432 MHz on a Bruker Avance III^{TM} HD 700 MHz (16.44 T magnetic field) spectrometer, using a 4 mm probe double-bearing probe, with 0.27 μs radio-frequency (rf) pulses (equivalent to a 10º tip angle), a recycle delay of 0.5 s, and a spinning rate of 15 kHz; chemical shifts are quoted in ppm from aqueous $Al(NO_3)_3$.

^{29}Si MAS NMR spectra were recorded at 79.495 MHz on a Bruker Avance III 400 MHz (9.4 T magnetic field) spectrometer, using a 7 mm probe double-bearing probe, with 2.4 μs (40º) rf pulses, a recycle delay of 60 s, and a spinning rate of 5 kHz; chemical shifts are quoted in ppm from tetramethylsilane (TMS). Cross-polarization ***(CP) ^{29}Si MAS***

NMR spectra were acquired on the same equipment, spinning rate and probe, with 3.5 μs ^1H 90° pulses, 8000 μs contact time and 5 s recycle delays.

Attenuated total reflectance (ATR) FT-IR spectra were recorded in reflection mode on a Unican Mattson Mod 7000 spectrometer equipped with a Specac Golden Gate Mk II ATR accessory fitted with a diamond top plate and KRS-5 focusing lenses (400-4000 cm^{-1}, 256 scans, 4 cm^{-1} resolution). Elemental analysis for C of the used desilicated catalysts were performed using a Leco Truspec 630-200-200 analyser.

The ***base properties*** of the materials were studied by ***temperature programmed desorption (TPD)*** *of* CO_2 (probe molecule), in a fixed-bed U-shaped Quartz flow reactor using a Micromeritics Autochem II Chemisorption Analyser. The sample (100 mg) was pre-treated *in situ* at 400 ºC (10 ºC min^{-1}) for 1 h, under He flow (50 mL min^{-1}). The reactor was cooled down to 100 ºC and then fed with a gas mixture composed of 10% CO_2 and 90% He (50 mL min^{-1}), for 1 h. Afterwards, the reactor was purged with He for 1 h to remove excess/physisorbed CO_2, and the sample was heated until 800 ºC (10 ºC min^{-1}) and the CO_2 desorbed analysed using a TCD detector. The amount of desorbed CO_2 was calculated via deconvolution of the TPD-CO_2 curves, and peak integration, using calibration curves.

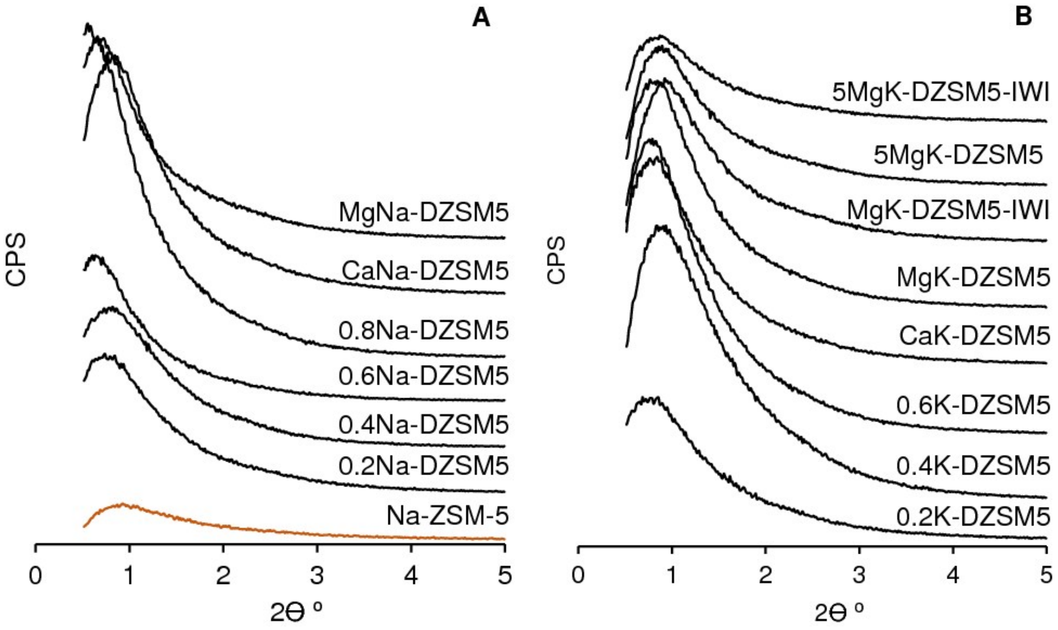

Figure S1. Low angle powder XRD patterns of the Na-containing (A) and K-containing (B) DZSM5 materials prepared via desilication (xM-DZSM5) and Me-impregnation. For comparison, zeolite Na-ZSM-5 is included.

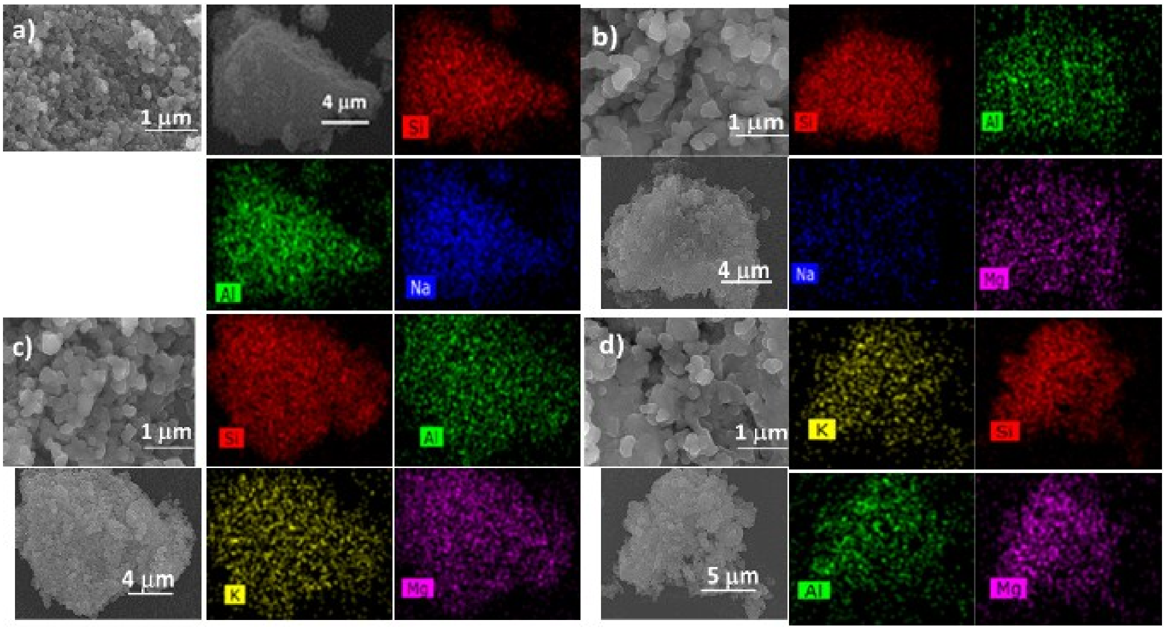

Figure S2. SEM images and elemental mappings of the materials 0.8Na-DZSM5 (a), MgNa-ZSM-5 (b), 5MgK-DZSM5 (d), 5MgK-DZSM5-IWI (e). In the elemental mappings, Si=red, Al=green, Na=dark blue, K=yellow, Mg=purple, Ca=light blue.

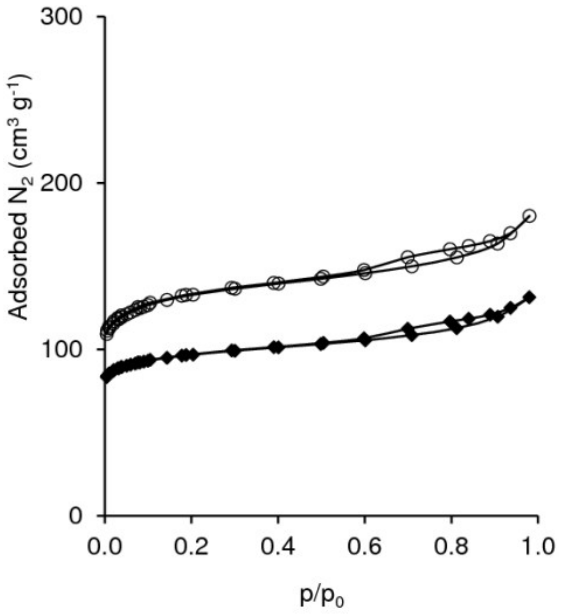

Figure S3. N_2 adsorption-desorption isotherms at -196 ºC of zeolites Na-ZSM-5 (o) and MgNa-ZSM-5 (♦).

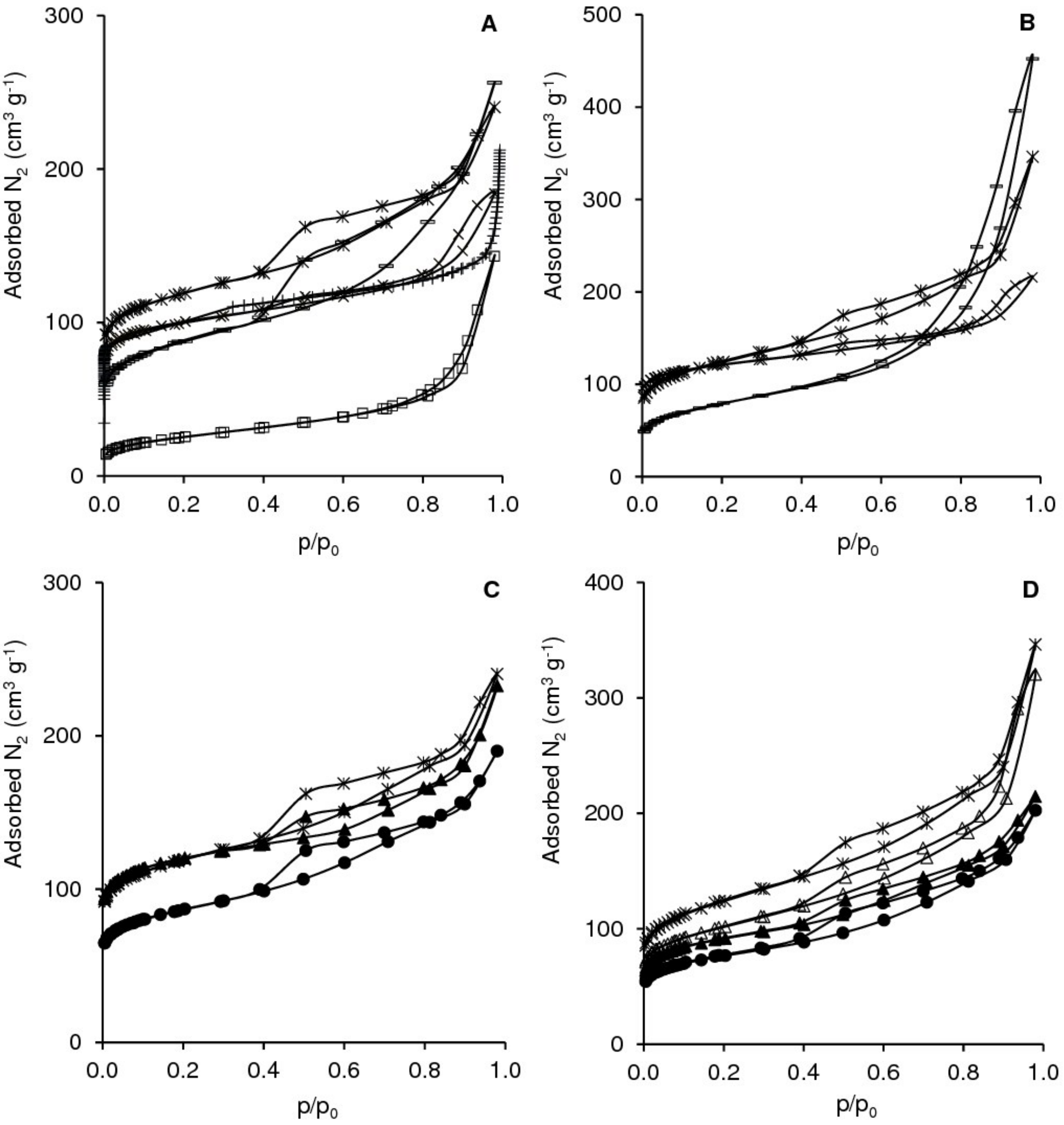

Figure S4. N$_2$ adsorption-desorption isotherms at -196 ºC of (**A**) ZSM-5 (+), 0.2Na-DZSM5 (×), 0.4Na-DZSM5 (*), 0.6Na-DZSM5 (–), 0.8Na-DZSM5 (□); (**B**) 0.2K-DZSM5 (×), 0.4K-DZSM5 (*), 0.6K-DZSM5 (–); (**C**) 0.4Na-DZSM5 (*), MgNa-DZSM5 (▲), CaNa-DZSM5 (●); (**D**) 0.4K-DZSM5 (*), MgK-DZSM5 (▲), MgK-DZSM5-IWI (Δ), CaK-DZSM5 (●).

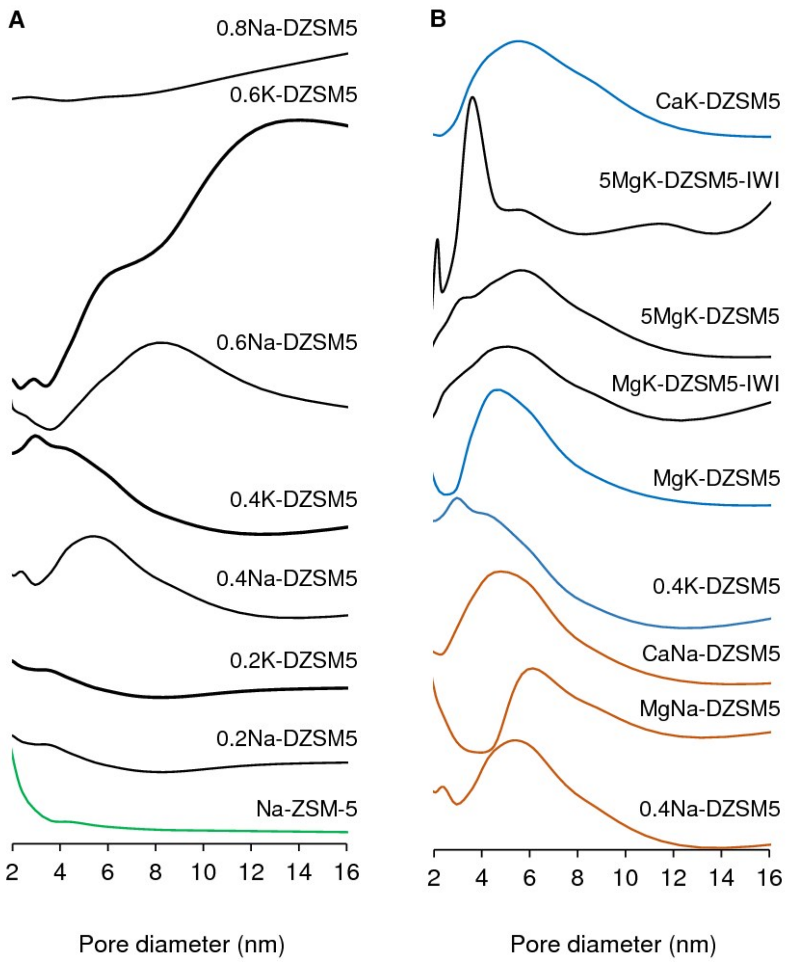

Figure S5. Mesopore size distribution curves for (A) desilicated xM-DZSM5 materials and (B) Me-containing DZSM5 materials and respective precursors 04M-DZSM5. (×), 0.4K-DZSM5 (*), 0.6K-DZSM5 (–); (D) 0.4K-DZSM5 (*), MgK-DZSM5 (▲), MgK-DZSM5-IWI (Δ), CaK-DZSM5 (●).

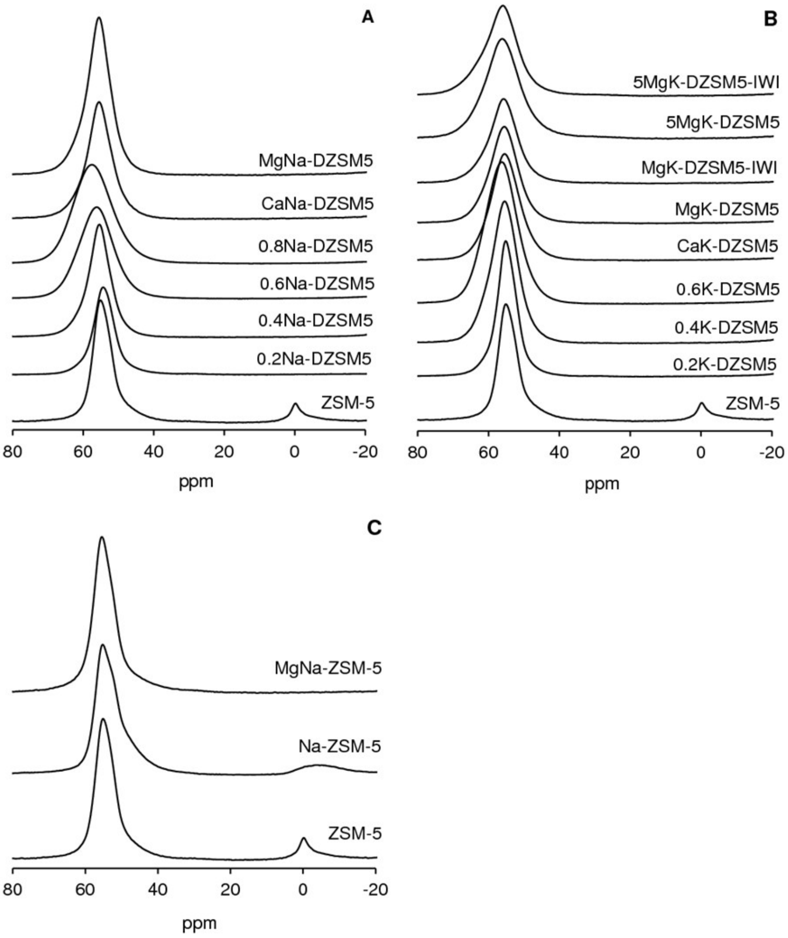

Figure S6. ^{27}Al MAS NMR spectra of the Na-containing (A) or K-containing (B) DZSM5 materials prepared via desilication (xM-DZSM5) and Me-impregnation. For comparison, zeolite ZSM-5 is included. ^{27}Al MAS NMR spectra of zeolites ZSM-5, Na-ZSM-5 and MgNa-ZSM-5 (C).

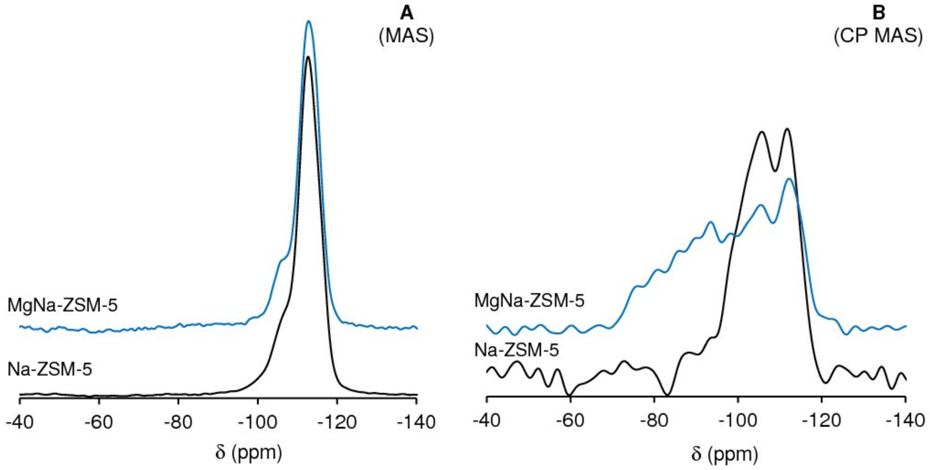

Figure S7. ^{29}Si MAS NMR (A) and ^{29}Si{^{1}H} CP MAS NMR (B) spectra of zeolites Na-ZSM-5 and MgNa-ZSM-5.

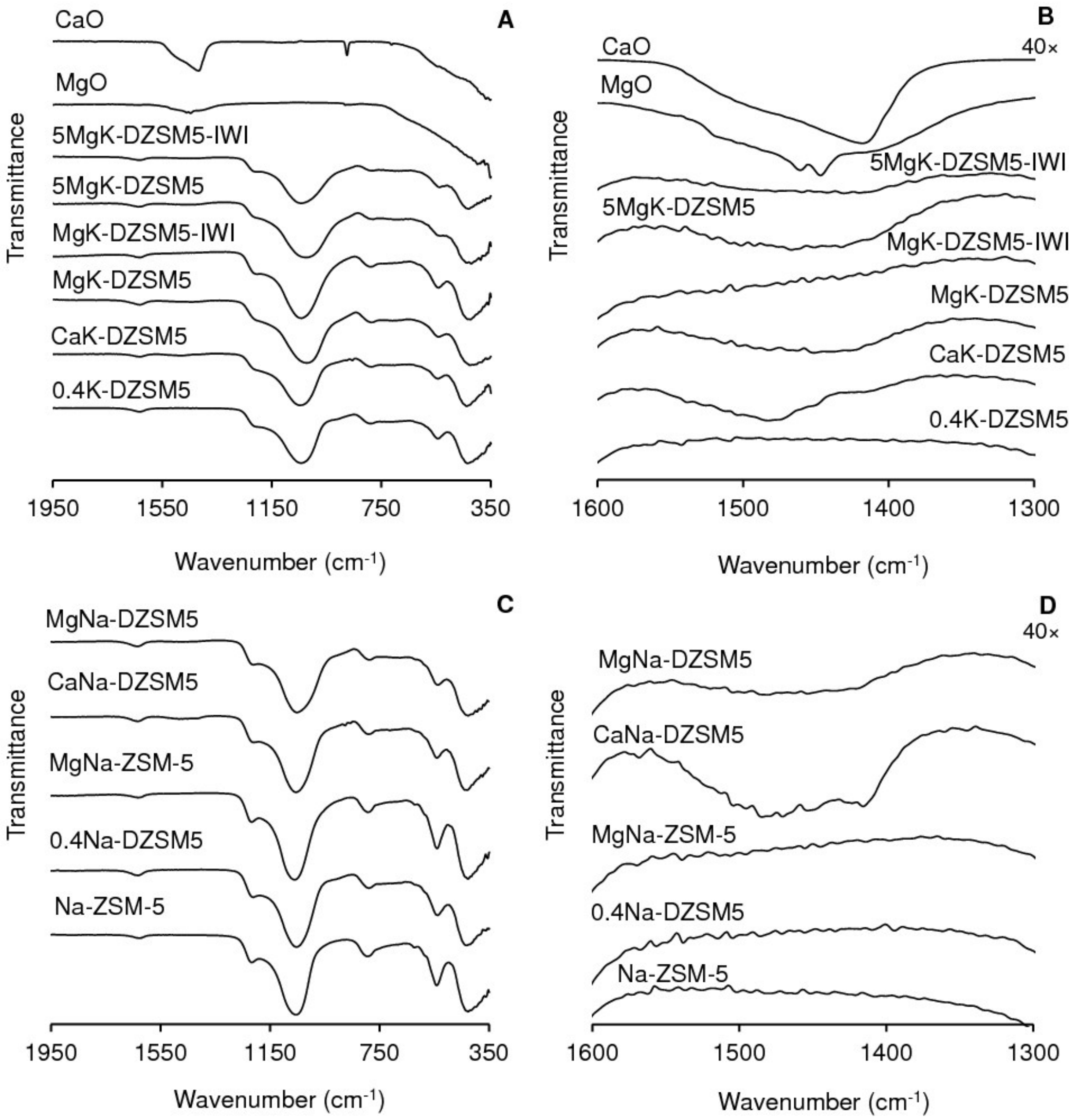

Figure S8. ATR FT-IR spectra of the DZSM5 family of desilicated materials; B and C are the spectra in the range 1300 to 1600 cm^{-1} (amplified 40×). For comparisons, the spectra of zeolites Na-ZSM-5 and MgNa-ZSM-5 (C, D), and bulk CaO and MgO (A, B) are included.

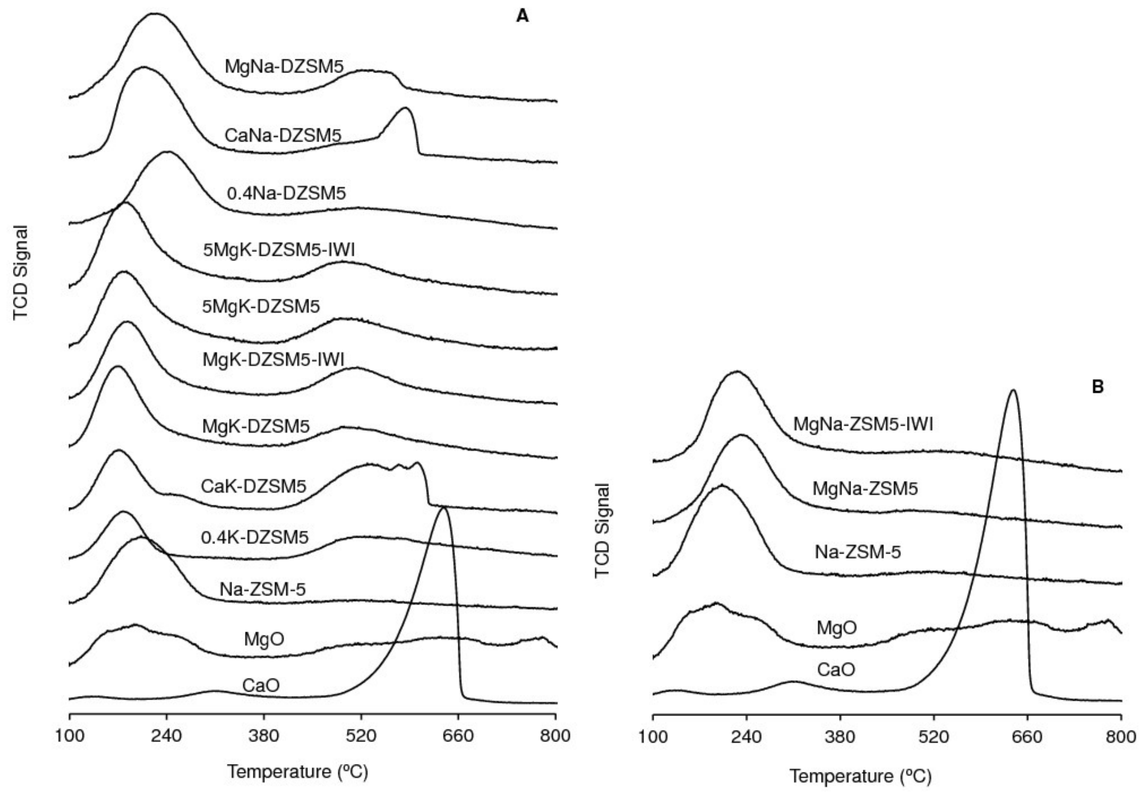

Figure S9. (A) CO_2-TPD profiles of the DZSM5 family of desilicated materials. Profiles for zeolite Na-ZSM5 and bulk CaO and MgO are included for comparison. (B) CO_2-TPD profiles of CaO, MgO and zeolites Na-ZSM-5, and MgNa-ZSM-5.

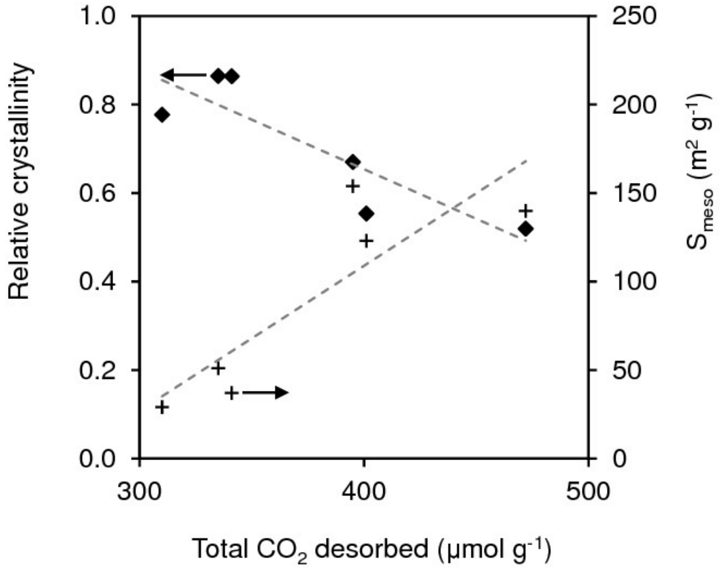

Figure S10. Relationship between the base properties (total amount of CO_2 desorbed) and the relative crystallinity and S_{meso} for the Na-containing zeolite and DZSM5 families of materials.

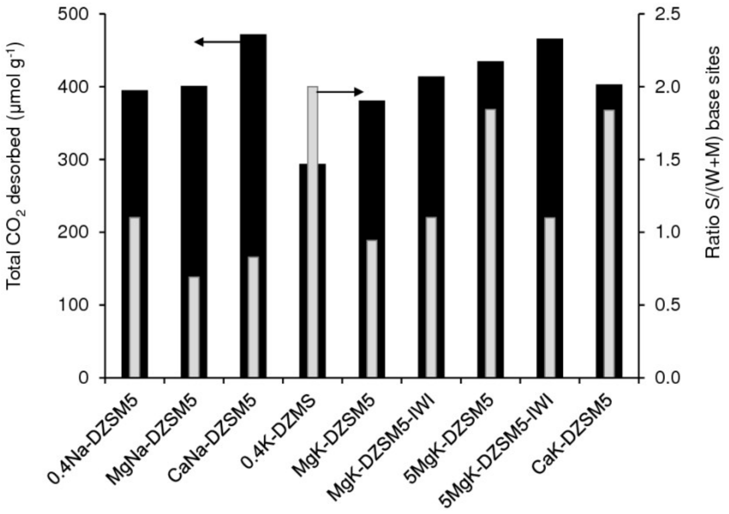

Figure S11. Base properties of the DZSM5 materials: total CO_2 desorbed (black bars) or molar ratio of S/(W+M) base sites (grey bars).

C. Catalytic studies

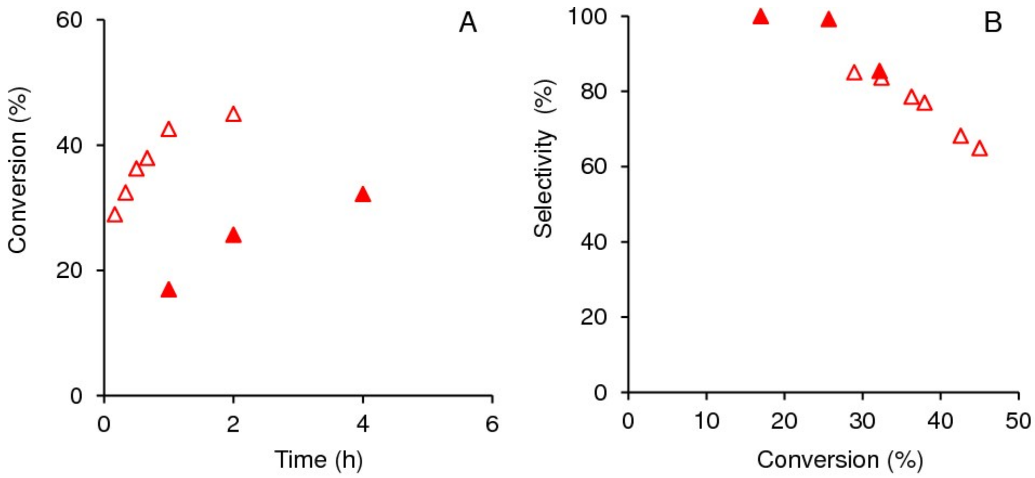

Figure S12. Influence of the Glu reaction temperature (75 (▲); 100 ºC (Δ)) on the catalytic performance of MgK-DZSM5. Reaction conditions: 0.28 M Glu in H_2O, 20 g_{cat} L^{-1} catalyst.

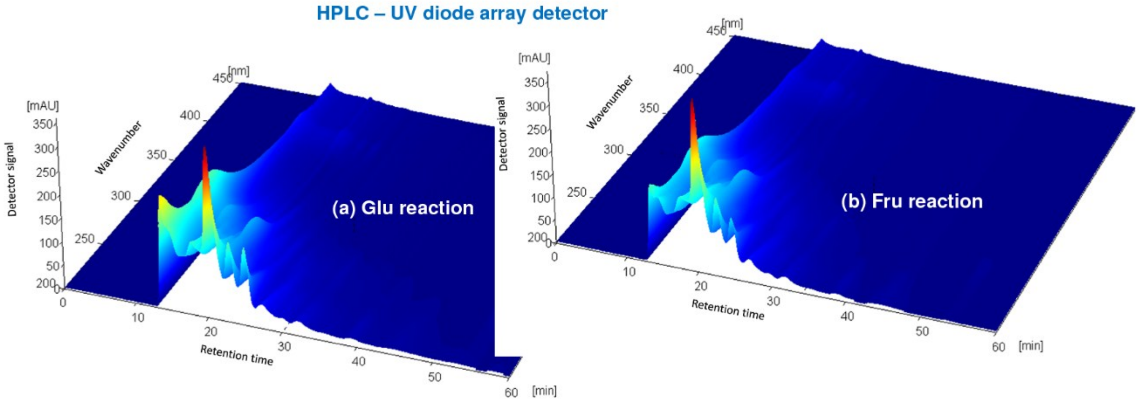

Figure S13. Three-dimensional chromatogram using a UV diode-array detector for the liquid phase of the reaction mixture using Glu or Fru as substrate and 5MgK-DZSM5 as catalyst. Reaction conditions: 0.28 M Glu in H_2O, 20 g_{cat} L^{-1} catalyst, 100 ºC, 2 h.

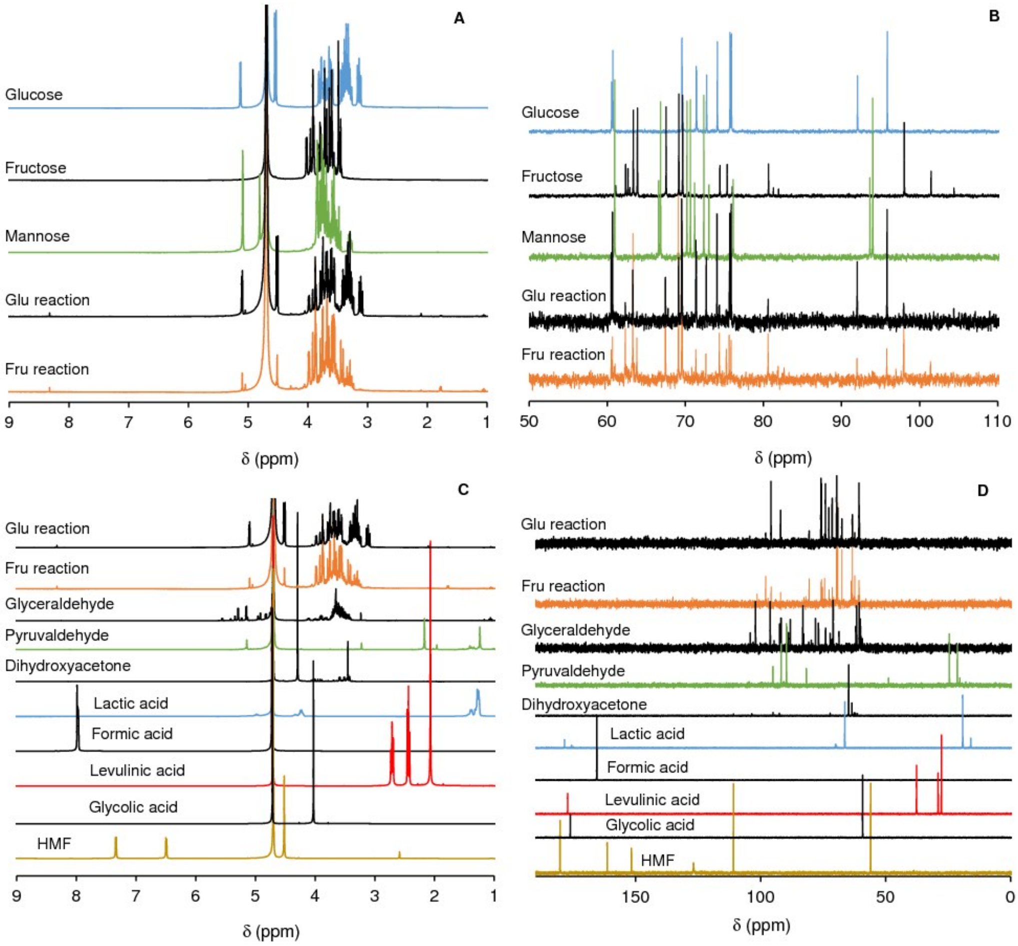

Figure S14. ^{1}H NMR (A, C) and ^{13}C NMR (B, D) spectra of the liquid phase of the reaction mixture for Glu or Fru as substrates. Standard spectra of hexoses (A, B) and potential by-products (C, D) are included for comparison (HMF=5-(hydroxymethyl)furfural). None of the products indicated in C and D could be clearly identified. Reaction conditions: 0.28 M Glu in D_2O, 20 g_{cat} L^{-1} catalyst MgK-DZSM5, 100 ºC, 2 h.

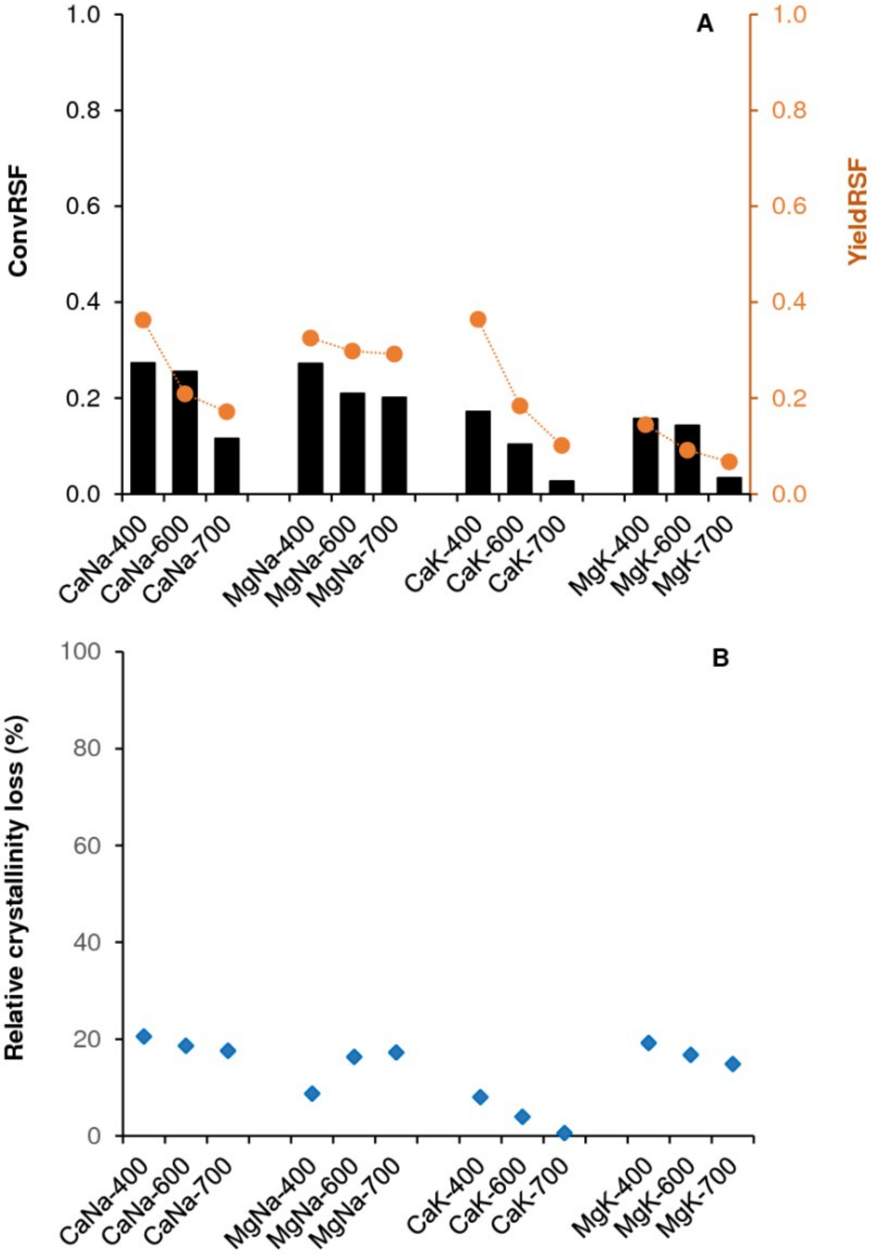

Figure S15. (A) Performance reduction and (B) loss of relative crystallinity of the materials MeM-DZSM5 used for Glu conversion and subsequently regenerated at 400, 600 or 700 ºC. ConvRSF and YieldRSF (A) denote the reducing scale factor (RSF, which ranges from zero for no drop in catalytic performance, to unity for complete loss of performance) for Glu conversion and Fru yield, respectively. Reaction conditions: 0.28 M Glu in H_2O, 20 g_{cat} L^{-1} catalyst, 100 ºC, 30 min.

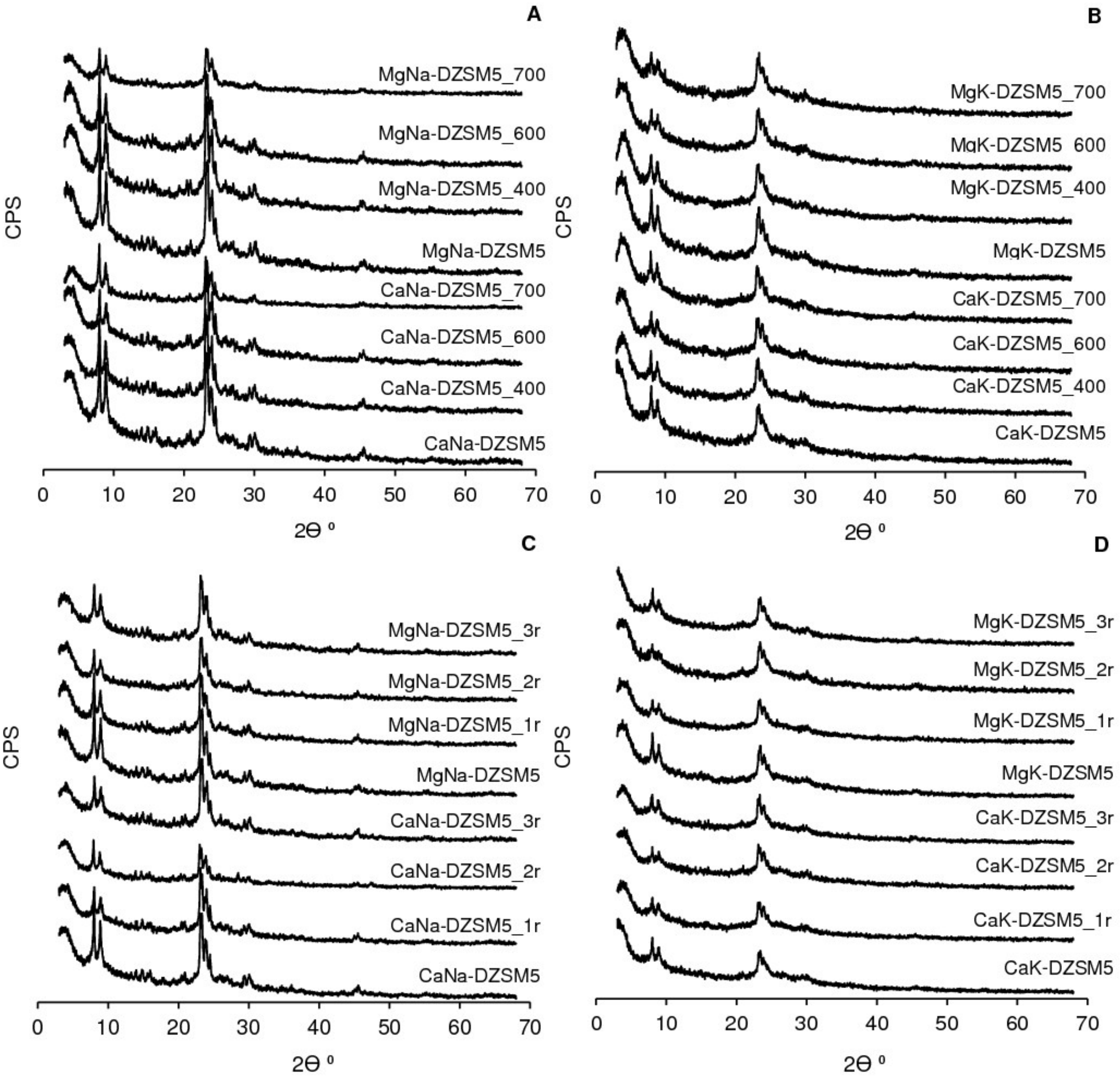

Figure S16. Wide angle powder XRD patterns of the MeM-DZSM5 materials before and after regeneration at different temperatures (A (M=Na), B (M=K)), or after recycling runs (C (M=Na), D (M=K)). In C and D, 1r, 2r and 3r denote the solids recovered after runs 1, 2 and 3, respectively. Reaction conditions of the used catalysts: 0.28 M Glu in H_2O, 20 g L^{-1} catalyst, 100 ºC, 30 min.

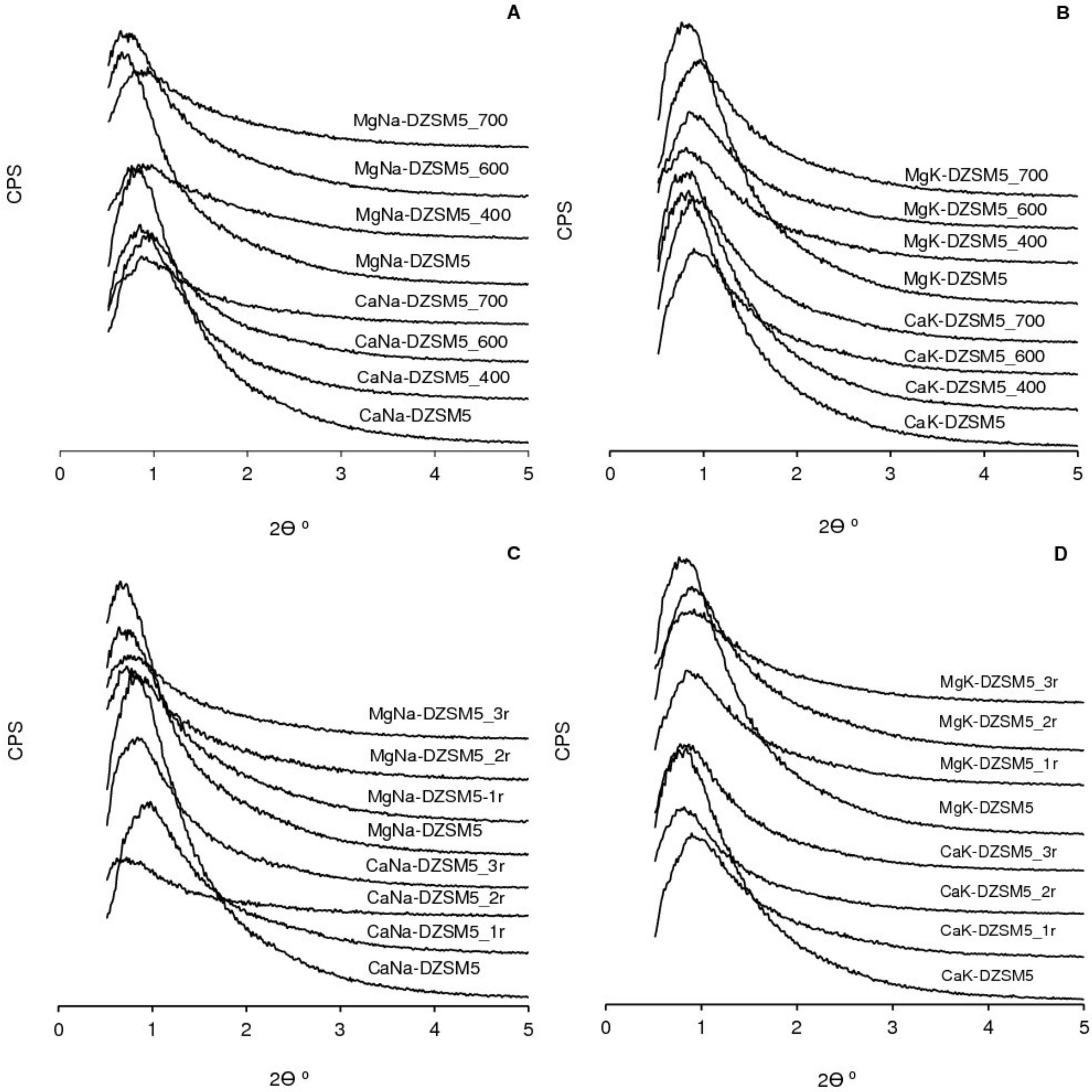

Figure S17. Low angle powder XRD patterns of the MeM-DZSM5 materials before and after regeneration at different temperatures (A, B), or after recycling runs (C, D). In C and D, 1r, 2r and 3r denote the solids recovered after runs 1, 2 and 3, respectively. Reaction conditions of the used catalysts: 0.28 M Glu in H_2O, 20 g L^{-1} catalyst, 100 ºC, 30 min.

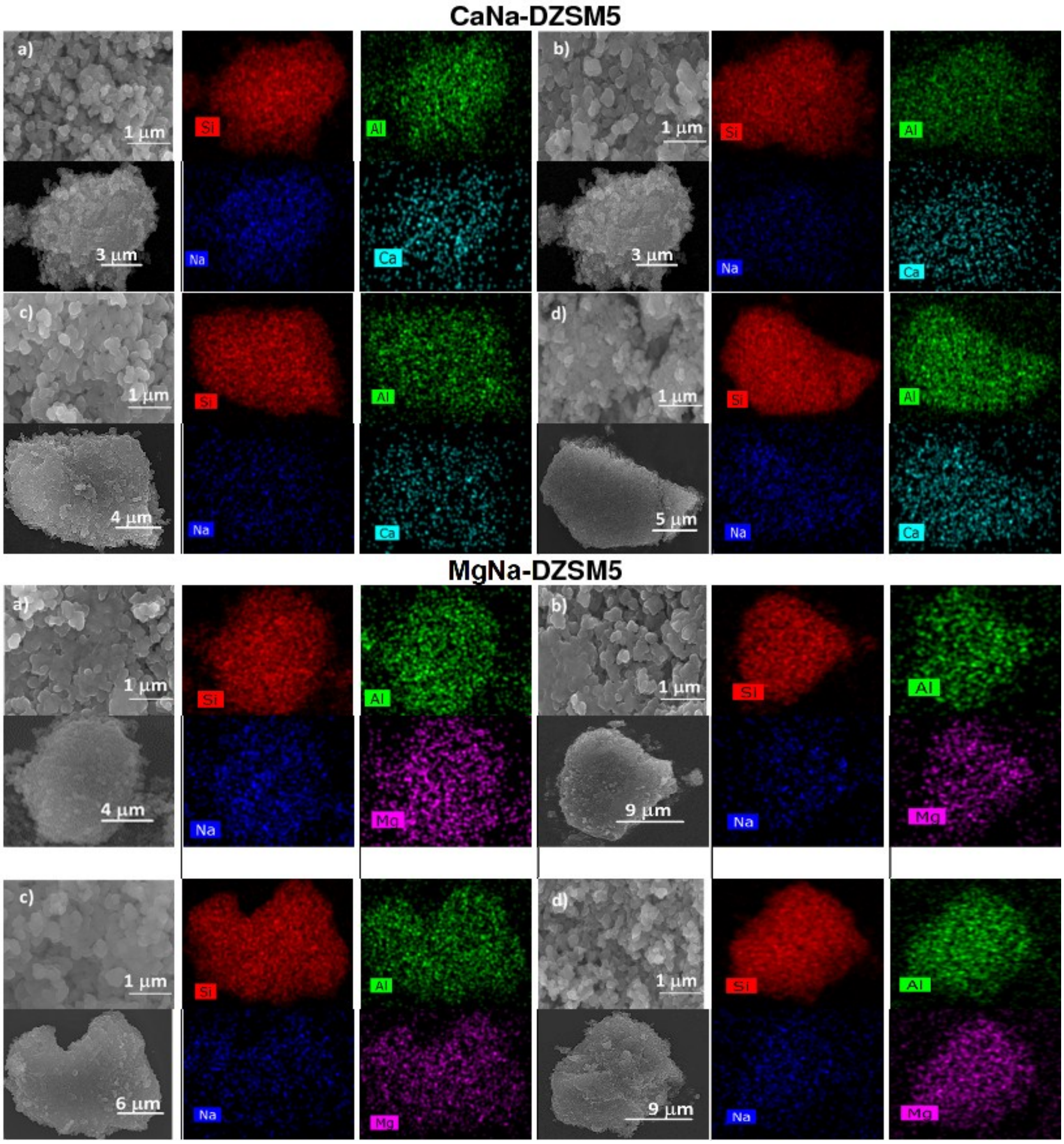

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Figure S18. SEM images and the respective elemental mappings of the materials CaNa-DZSM5, MgNa-DZSM5, CaK-DZSM5, MgK-DZSM5 before use (a) and after the 1st run (b), 2nd run (c) and 3rd run (d). For the elemental mappings: Si = red, Al = green, Na = dark blue, K = yellow, Mg = purple, Ca = light blue.