Electronic Supplementary Information

Synthesis of catalysts

Sulphated zirconia (SO_4^2/ZrO_2) was synthesised following the procedure of Palacios-Grijalva.¹ Zirconium *n*-propoxide (20 mL, 70 wt% in *n*-propanol) was added to 30 mL of isopropanol and stirred at room temperature. Next, a sulphuric acid solution (1 mL 95% sulphuric acid in 3.2 mL distilled water) was added dropwise to the solution. The obtained solid was filtered and dried at 60 °C, followed by a calcination in a shallow bed in a porcelain crucible under static air with a linear rate of 1 °C/min and kept for 6 h at 600 °C.

Zr-Beta was prepared via a two steps synthesis from a Zeocat PB65H H-Beta zeolite. First, 1 g of zeolite PB65H was deeply dealuminated by stirring it at 100 °C in a strong acidic medium (50 mL of 13 M HNO₃) for 20 hours. Next, the solids were filtered, repeatedly washed with water and dried. Second, 0.2 g of the deeply dealuminated Zeocat PB65H H-Beta zeolite is deeply grinded with 0.1 mmol of a $Zr(acac)_4$ precursor in a mortar. Afterwards the material is calcined in a shallow bed in a porcelain crucible under static air with a linear rate of 1 °C/min to 550 °C and kept for 2 hours at 550 °C.

²⁷Al liquid NMR

²⁷Al liquid NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer equipped with a sample case and a 5 mm BBO BB-1H probe with z-gradients. Sample preparation included transfer of 300 μL of the crude reaction mixture and 300 μL of D₂O in an NMR tube. To measure ²⁷Al NMR spectra, the Larmor frequency of ¹³C (75.468 MHz) was selected, which was adjusted to the Larmor frequency of ²⁷Al (78.204 MHz) by tuning and matching. The optimisation of the zg pulse programme was performed manually resulting in following parameters: p1 7.00 μs; ds 0; ns 128; d1 0.1 s; aq 0.33 s; sw 320 ppm.

Quantification of the compounds of the reaction mixture

A known amount of maleic acid was used as an external standard for the ¹H-NMR quantification, where the singlet of maleic acid at 5.998 ppm was used for calibration. Citric acid (after acidification, *vide infra*) was quantified based on its signal at 2.96 ppm (2 protons); PTA was quantified based on its signal at 3.24 ppm (1 proton, quintet) and MSA was quantified using the signal at 1.21 ppm (3 protons, doublet). The products obtained via radical fragmentation were quantified using the signal at 2.10 ppm (3 protons, singlet) for acetic acid and 2.23 ppm (6 protons, singlet) for acetone.

Determination of the amount of citric acid and citrate

When zeolite materials were applied in the catalytic reactions, new peaks and shoulders emerged in the ¹H-NMR spectrum of the crude reaction mixture (Figure S1, region 2.70 - 2.90 ppm). However, none of the possible side products identified in Scheme 1 would give a match with these chemical shifts. After acidifying this crude reaction mixture with an aqueous HCl solution (2 M HCl in H₂O), the unidentified peaks reverted to those of citric acid, indicating that part of citric acid was present in a deprotonated form (Table S1, Figure S2). Since the pH of the crude reaction mixture is between 2 and 3, this citrate will predominantly consist of dihydrogen citrate (CitH₂⁻). Further analysis of the crude reaction mixture by ²⁷Al-NMR confirmed the presence of Al-citrate with a broad band at 9.2 ppm, which could be interpreted as a superposition of 1:1 and 2:1 complexes of CitH₂⁻ and Al.² The sharp peak at 0.2 ppm represents hydrolysed aluminum.³ From the NMR spectra, it seems that only citrate is prone to form Al complexes, while 3-carboxy-1,5-pentanedioate (deprotonated PTA) remains unaffected by the presence of Al. This can be explained by the involvement of the tertiary hydroxyl group in the chelation of citrate with Al, which makes Al citrate a 270 times stronger complex than the Al 3-carboxy-1,5-pentanedioate complex.⁴



Figure S1. ¹H-NMR spectrum of citric acid (black), PTA (blue) and a crude reaction mixture (red). Reaction conditions: 0.1 g H-Beta 12.5, 0.5 mol % Pd (5 wt% Pd/C), 150 °C, 16 h, 10 bar H₂.

Table S1. Substrate and product distribution of a crude reaction prior to and after acidifying with an aqueous HCl solution.

	Distribution (%)							
	Citric Acid	Citrate	ΡΤΑ	MSA	Fragmentation			
Crude reaction mixture ^a	18	24	56	1	< 1			
Acidified reaction mixture ^b	43	< 1	55	1	< 1			

^{*a*} Reaction conditions: 0.1 g H-Beta 12.5, 0.5 mol % Pd (5 wt% Pd/C), 150 °C, 16 h, 10 bar H₂. ^{*b*} 200 μL of the crude reaction mixture acidified with 200 μL of 2 M HCl in water solution.



δ [ppm]

Figure S2. ¹H-NMR spectrum of a crude reaction mixture (red) and the same reaction mixture after acidifying with a 2 M HCl in H_2O solution. Reaction conditions: 0.1 g H-Beta 12.5, 0.5 mol % Pd (5 wt% Pd/C), 150 °C, 16 h, 10 bar H_2 .



Figure S3. ²⁷Al-NMR spectrum of the reaction mixture mentioned in Figure S2. NMR resonance peak assignments: 0.2 ppm, Al monomeric species; 9.2 ppm, 1:1 Al:CitH₂⁻ and/or 1:2 Al:CitH₂⁻.^[1,2]

Variation of different parameters

				Distribution [%] ^b			Selectivity [%]		
	Zeolite	Si/Al	Amount [g]	Citric acid	Citrate ^c	X [%] ^d	PTA^e	MSA ^f	Fragm. ^g
1	H-Y	2.7	0.02	15	33	53	95	4	2
2	H-Y	2.7	0.06	11	51	38	98	1	1
3	H-Y	2.7	0.10	7	53	40	95	< 1	5
4	H-Beta	10.8	0.02	71	< 1	28	96	1	2
5	H-Beta	10.8	0.06	47	18	36	97	2	< 1
6	H-Beta	10.8	0.10	33	20	47	97	1	1
7	H-Beta	10.8	0.12	29	26	46	98	1	1
8	H-Beta	12.5	0.02	63	8	29	96	2	2
9	H-Beta	12.5	0.06	40	19	41	98	1	< 1
10	H-Beta	12.5	0.10	26	30	44	99	1	< 1
11	H-Beta	12.5	0.12	18	33	49	99	1	< 1

Table S2. Variation of the amount of zeolite dehydration catalyst. ^a

^a Reaction conditions: citric acid (0.2 mmol), water (2 mL), 0.5 mol% Pd (5 wt% Pd/C), 140 °C, 10 bar H₂, 20 h. ^b Distribution of the reactants, consisting of citric acid and Al-citrate, after reaction. The sum of both represents the total amount of unreacted substrate. ^c The amount of citric acid that is present as Al-citrate determined by ¹H-NMR after acidifying the mixture. ^d Conversion *i.e.* the amount of citric acid and citrate that has reacted. ^e Propane-1,2,3-tricarboxylic acid. ^f Methylsuccinic acid. ^g Fragmentation products, which are represented by acetone and acetic acid.

Table S3. Variation of the amount of Pd/C. ^a

					Distribution [%] ^c		_	Selectivity [%]		
	Zeolite	Si/Al	Amount [g]	Pd/C [mol%] ^b	Citric acid	Citrate ^d	X [%] ^e	PTA ^f	MSA^g	Fragm. ^h
1	H-Beta	10.8	0.1	0.5	3	18	80	96	3	< 1
2	H-Beta	10.8	0.1	0.25	4	24	72	96	4	< 1
3	H-Beta	10.8	0.1	0.1	4	22	75	90	9	1
4	H-Beta	10.8	0.1	0.05	9	27	65	86	14	< 1

^{*a*} Reaction conditions: citric acid (0.2 mmol), water (2 mL), 150 °C, 10 bar H₂, 20 h. ^{*b*} mol% of Pd (5 wt% Pd/C) with respect to citric acid. ^{*c*} Distribution of the reactants, consisting of citric acid and Al-citrate, after reaction. The sum of both represents the total amount of unreacted substrate. ^{*d*} The amount of citric acid that is present as Al-citrate determined by ¹H-NMR after acidifying the mixture. ^{*e*} Conversion *i.e.* the amount of citric acid and citrate that has reacted. ^{*f*} Propane-1,2,3-tricarboxylic acid. ^{*g*} Methylsuccinic acid. ^{*h*} Fragmentation products, which are represented by acetone and acetic acid.

Table S4. Variation of H₂ pressure.^{*a*}

					Distribution [%] ^b		_	Selectivity [%]		
	Zeolite	Si/Al	Amount [g]	P _{H2} [bar]	Citric acid	Citrate ^c	X [%] ^d	PTA ^e	MSA ^f	Fragm. ^g
1	H-Beta	10.8	0.1	10	3	18	80	96	3	< 1
2	H-Beta	10.8	0.1	8	3	14	83	90	9	< 1
3	H-Beta	10.8	0.1	6	8	21	71	94	6	< 1
4	H-Beta	10.8	0.1	4	9	21	71	90	9	< 1

^{*a*} Reaction conditions: citric acid (0.2 mmol), water (2 mL), 0.5 mol% Pd (5 wt% Pd/C), 150 °C, 20 h. ^{*b*} Distribution of the reactants, consisting of citric acid and Al-citrate, after reaction. The sum of both represents the total amount of unreacted substrate. ^{*c*} The amount of citric acid that is present as Al-citrate determined by ¹H-NMR after acidifying the mixture. ^{*d*} Conversion *i.e.* the amount of citric acid and citrate that has reacted. ^{*e*} Propane-1,2,3-tricarboxylic acid. ^{*f*} Methylsuccinic acid. ^{*g*} Fragmentation products, which are represented by acetone and acetic acid.

Table S5. Recycling of the catalytic system. ^a

			Distribution [%] ^b			Selectivity [%]		
	Zeolite	Calcination prior to reuse	Citric acid	Citrate ^c	X [%] ^d	PTA ^e	MSA ^f	Fragm. ^g
1	Fresh	/	3	18	80	96	3	< 1
2	Reuse 1	No	26	7	67	89	11	< 1
3	Reuse 2	No	49	6	45	92	7	< 1
4	Reuse 1	Yes	16	11	73	97	3	< 1
5	Reuse 2	Yes	37	8	52	96	4	< 1
6	Realuminated	/	7	21	72	95	4	< 1

^{*a*} Reaction conditions: citric acid (0.2 mmol), water (2 mL), 0.1 g of zeolite, 0.5 mol% Pd (5 wt% Pd/C), 150 °C, 20 h. ^{*b*} Distribution of the reactants, consisting of citric acid and Al-citrate, after reaction. The sum of both represents the total amount of unreacted substrate. ^{*c*} The amount of citric acid that is present as Al-citrate determined by ¹H-NMR after acidifying the mixture. ^{*d*} Conversion *i.e.* the amount of citric acid and citrate that has reacted. ^{*e*} Propane-1,2,3-tricarboxylic acid. ^{*f*} Methylsuccinic acid. ^{*g*} Fragmentation products, which are represented by acetone and acetic acid.

		Chemical shift (ppm)	Fraction (%)
	Si(OSi) ₂ (OH) ₂	-92,7	12,4
Realuminated	Si(OSi) ₃ (OH)	-99,5	18,3
	$Si(OSi)_{4-n}(OAI)_n$ (n = 1,2)	-101,9	3,2
	$Si(OSi)_{4-n}(OAI)_n$ (n = 1)	-105,6	16,7
	Si(OSi) ₄	-110,6	5,0
	Si(OSi) ₄	-114,3	2,9
		Chemical shift (ppm)	Fraction (%)
	Si(OSi) ₂ (OH) ₂	-92,7	3,6
Dealuminated	Si(OSi) ₃ (OH)	-99,5	8,3
Dealuminated	$Si(OSi)_{4-n}(OAI)_n$ (n = 1,2)	-101,9	3,1
	$Si(OSi)_{4-n}(OAI)_n$ (n = 1)	-105,6	4,0
	Si(OSi) ₄	-110,6	2,0
	Si(OSi) ₄	-114,3	0,7
		Chemical shift (ppm)	Fraction (%)
2	Si(OSi) ₂ (OH) ₂	-92,7	3,3
\wedge	Si(OSi) ₃ (OH)	-99,5	12,1
Fresh	$Si(OSi)_{4-n}(OAI)_n$ (n = 1,2)	-101,9	15,4
	$Si(OSi)_{4-n}(OAI)_n$ (n = 1)	-105,6	5,7
	Si(OSi) ₄	-110,6	6,4
	Si(OSi) ₄	-114,3	2,1
-80 -90 -100 -110 -120 -130 ²⁹ Si chemical shift (ppm)			

¹H-²⁹Si Cross Polarization Magic Angle Spectroscopy (CPMAS)

Figure S4. ¹H-²⁹Si CPMAS NMR spectra and their decompositions into contribution of Si from different environments (proportional to the respective ²⁹Si MAS NMR spectrum) of the fresh H-Beta 10.8 (bottom), the twice reused and calcined, dealuminated H-Beta (middle) and the realuminated H-Beta catalyst (top). The black curve represents the measured NMR spectrum and the red dashed curve represents the modeled spectrum.

Calculation of framework and total Si/Al ratios from MAS NMR data

The framework Si/Al ratio of the fresh H-Beta 10.8 ((Si/Al_{Fr})_{Fresh}) was estimated from the contribution of Si(OSi)₃(OAI) and Si(OSi)₂(OAI)₂ environments in the respective ²⁹Si MAS NMR spectrum (Figure 3). In this spectrum, the signal at -105.6 ppm can be assigned to Si(OSi)₃(OAI), while the signal at -101.9 is a superposition of contributions of Si(OSi)₃(OAI) and Si(OSi)₂(OAI)₂, which are undistinguishable from each other. If a random incorporation of Al into the framework T sites of the H-Beta 10.8 zeolite is assumed, one can derive the probability (p_{Si}) that a T site is occupied by a Si atom from the summed intensity of the Si(OSi)₄(I_{4Si}) signals:

$$(p_{Si})^4 = I_{4Si} = 0.46 + 0.22 = 0.68$$

 $p_{Si} = 0.91$

Thus the probability that a T site is occupied by a Al atom is then:

$$p_{Al} = 1 - p_{Si} = 0.09$$

Using these probabilities, a prediction can be made about the intensities I_{3Si1AI} and I_{2Si2AI} .

$$I_{3Si1Al} = 4 * p_{Si}^{3} * p_{Al} = 4 * 0.91^{3} * 0.09 = 0.27$$
$$I_{2Si2Al} = 6 * p_{Si}^{2} * p_{Al}^{2} = 6 * 0.91^{2} * 0.09^{2} = 0.04$$

The sum of the predicted intensities I_{3Si1AI} and I_{2Si2AI} matches the sum of the intensities that are observed at -101.9 ppm and -105.6 ppm in the ²⁹Si MAS NMR spectrum of the fresh H-Beta zeolite, supporting the hypothesis of a random incorporation of AI at the different T sites in the fresh H-Beta zeolite. Using these predicted intensities, the framework Si/AI ratio of the fresh H-Beta 10.8 zeolite ((Si/AI_{Fr})_{Fresh}) is obtained *via* following formula:⁵

$$\left(\frac{Si}{Al_{Fr}}\right)_{Fresh} = \frac{I_{Si}}{0.25 * I_{3Si1Al} + 0.5 * I_{2Si2Al}} = \frac{1}{0.25 * 0.27 + 0.5 * 0.04} = 11.4$$

Assuming that the amount of silicon atoms remains constant during the process of dealumination and realumination, the framework Si/Al ratio of the twice reused and calcined, dealuminated H-Beta ($(Si/Al_{Fr})_{Dealum}$) and the realuminated H-Beta ($(Si/Al_{Fr})_{Realum}$) can be calculated from the normalised framework AI ($Al_{Norm-Fr}$) of the respective samples:

$$\begin{pmatrix} Si \\ Al_{Fr} \end{pmatrix}_{Dealum} = \begin{pmatrix} Si \\ Al_{Fr} \end{pmatrix}_{Fresh} * \frac{(Al_{Norm-Fr})_{Fresh}}{(Al_{Norm-Fr})_{Dealum}}$$
$$\begin{pmatrix} Si \\ Al_{Fr} \end{pmatrix}_{Realum} = \begin{pmatrix} Si \\ Al_{Fr} \end{pmatrix}_{Fresh} * \frac{(Al_{Norm-Fr})_{Fresh}}{(Al_{Norm-Fr})_{Realum}}$$

The total framework Si/Al (Si/Al_{tot}) of a zeolite sample can be calculated from its (Si/Al_{Fr}) by taking the amount of normalised framework Al (Al_{Norm-Fr}) and extra-framework Al (Al_{Norm-EF}) obtained from the ²⁷Al MAS NMR spectra into account:

$$\frac{Si}{Al_{Tot}} = \left(\frac{Si}{Al_{Fr}}\right) / \left(1 + \frac{Al_{Norm - EF}}{Al_{Norm - Fr}}\right)$$

XRD Analysis



Figure S5. XRD patterns of the fresh H-Beta 10.8 (black), twice reused and calcined, dealuminated H-Beta (red) and realuminated H-Beta catalyst (blue).

References supplementary information

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