Supporting Information

Design of Base Zeolite Catalysts by Alkali-Metal Grafting in Alcoholic Media

Tobias C. Keller, Kartikeya Desai, Sharon Mitchell, and Javier Pérez-Ramírez*

Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland.

*Corresponding author. E-mail: jpr@chem.ethz.ch.

Table S1. Treatment conditions and characterization data of the USY zeolite catalysts.

Zeolite	c_{MOH}[a] (M)	Cation[b]	Solvent	V_{pore} ($cm^3\ g^{-1}$)	V_{micro}[c] ($cm^3\ g^{-1}$)	S_{ext}[c] ($m^2\ g^{-1}$)	S_{BET}[d] ($m^2\ g^{-1}$)	Crystallinity[e] (%)	M/Si ratio[f] (mol mol^{-1})
SiUSY	as received		-	0.56	0.30	117	693	100	-
	0	-	MeOH	0.54	0.29	101	662	100	0
	0.025	Na^+	MeOH	0.52	0.29	83	634	97	0.0050
	0.05	Na^+	MeOH	0.52	0.29	82	646	97	0.0067
	0.075	Na^+	MeOH	0.51	0.29	70	621	98	0.022
	0.1	Na^+	MeOH	0.51	0.29	70	615	97	0.022
	0.15	Na^+	MeOH	0.51	0.28	69	615	94	0.026
	0.2	Na^+	MeOH	0.34	0.10	48	253	64	0.071
	0.05	Na^+	EtOH	0.44	0.23	56	498	70	0.057
	0.1	Na^+	EtOH	0.25	0.10	34	225	30	0.078
	0.05	Na^+	*i*PrOH	0.37	0.16	45	355	40	0.10
	0.1	Na^+	*i*PrOH	0.16	0.07	18	164	24	0.15
	0.1	Li^+	MeOH	0.55	0.28	117	650	100	0.016
	0.05	K^+	MeOH	0.64	0.28	85	638	95	0.034
	0.1	K^+	MeOH	0.51	0.27	67	590	72	0.075
	0.05	Rb^+	MeOH	0.46	0.25	61	531	68	0.059
	0.1	Rb^+	MeOH	0.44	0.23	50	502	52	0.090
	0.025	Cs^+	MeOH	0.49	0.28	65	595	72	0.029
	0.05	Cs^+	MeOH	0.46	0.24	53	529	45	0.053
	2% Na^+ (dry impregnation)			0.34	0.10	23	240	30	-
AlUSY15	as received		-	0.54	0.54	144	760	100	-
	0.1	Na^+	MeOH	0.53	0.53	163	727	100	0.033
AlUSY30	as received		-	0.56	0.56	171	797	100	-
	0.1	Na^+	MeOH	0.54	0.54	202	726	100	0.030
SiO_2	as received		-	0.72	0.0	479	479	-	-
	0.1	Na^+	MeOH	0.59	0.0	320	328	-	0.024

[a] Metal hydroxide (MOH) concentration. [b] Cation of the hydroxide salt. [c] *t*-plot method. [d] BET method. [e] XRD. [f] Na, Li: ICP-OES; Si, K, Rb, Cs: XRF.

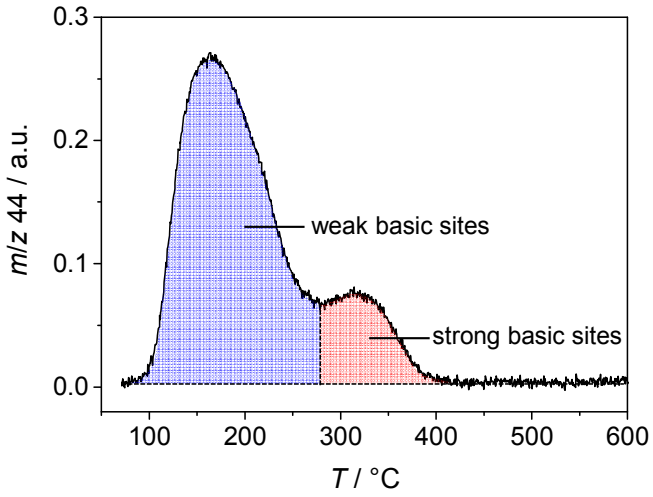

Figure S1. Quantification of the relative number of weak and strong basic sites in the metal-grafted zeolites by CO_2-TPD. The concentrations were calculated by integrating the respective contributions below and above 280°C in the desorption profile, as exemplified for the FAU405 zeolite alkaline treated with NaOH (0.1 M) in methanol.

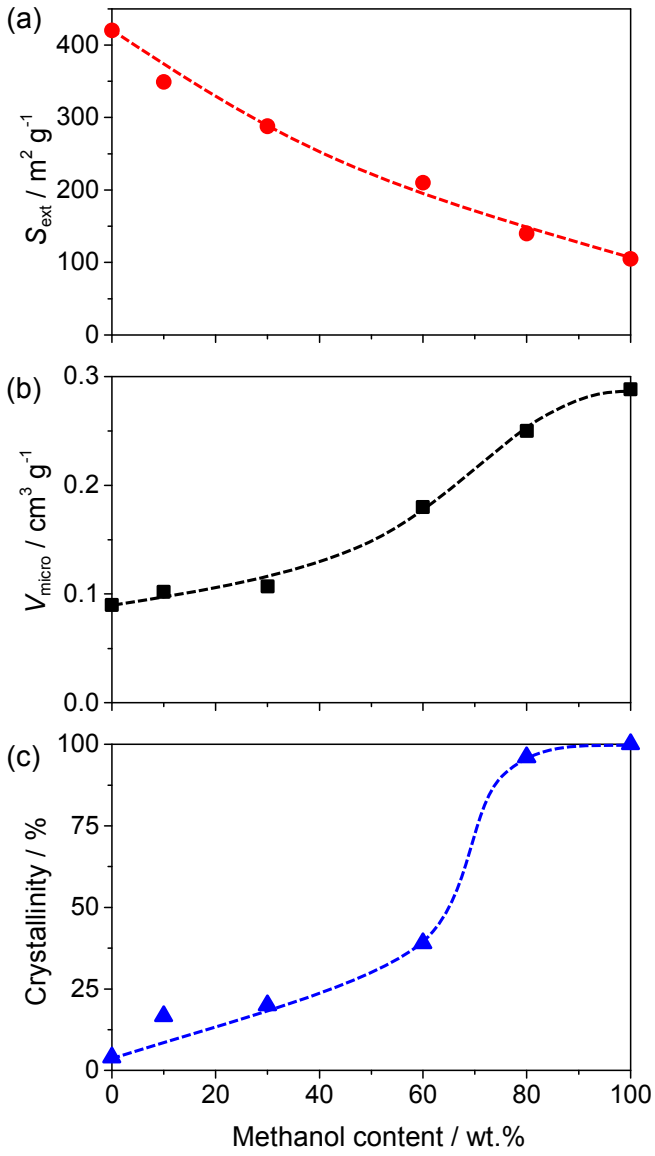

Figure S2. (a) External surface area, (b) micropore volume, and (c) crystallinity of SiUSY zeolites alkaline treated with NaOH (0.05 M) in MeOH:H_2O mixtures of different composition.

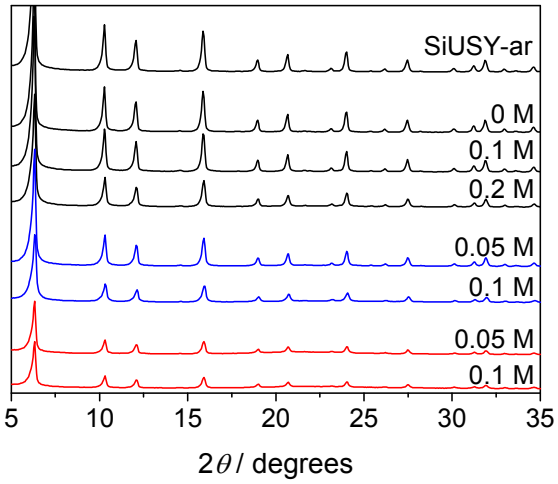

Figure S3. X-ray diffractograms of SiUSY zeolites as-received and NaOH-treated at different concentrations in MeOH (black), EtOH (blue), and *i*PrOH (red).

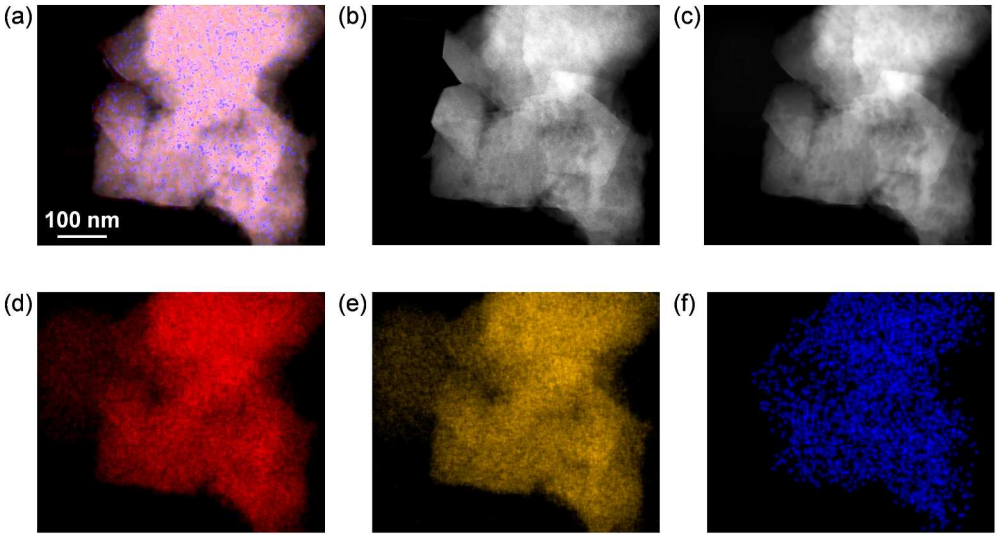

Figure S4. Supporting images for (a) the elemental map of silicon (pink) and sodium (blue) of the NaOH-treated (0.1 M in MeOH) SiUSY zeolite presented in Figure 3; HAADF-STEM images of the sample (b) before and (c) after the EDX analysis. Individual elemental maps of (d) silicon, (e) oxygen, and (f) sodium. The scale bar in (a) applies to all images.

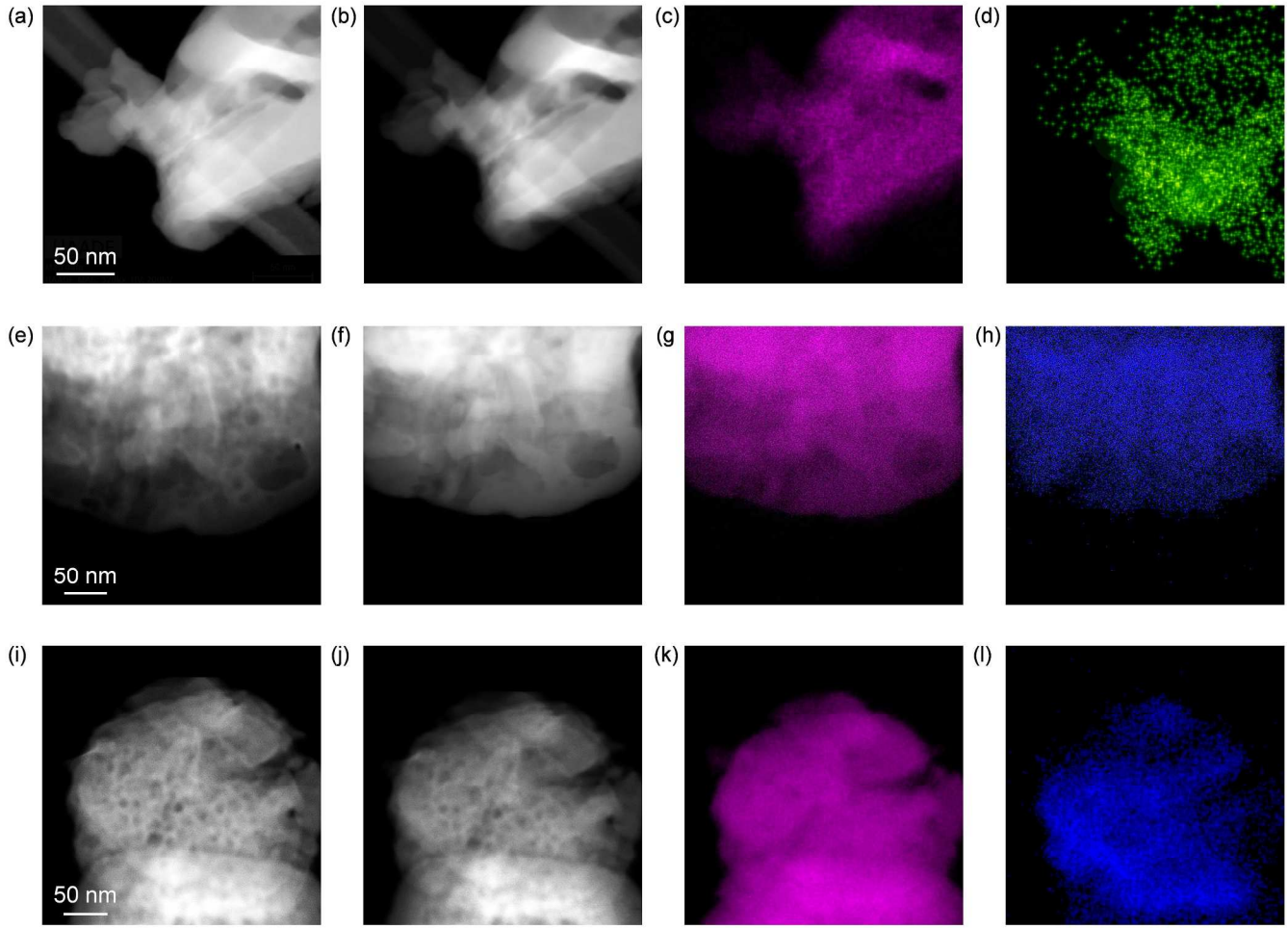

Figure S5. Supporting images for the elemental maps of (a-d) the RbOH-treated (0.05 M in MeOH) and (e-l) the KOH-treated (0.05 M in MeOH) SiUSY zeolites presented in Figure 8; HAADF-STEM images of the sample (a,e,i) before and (b,f,j) after the EDX analysis. Individual elemental maps of (c,g,k) silicon and (d) rubidium or (h,l) potassium. The scale bars apply to all images in the same row.

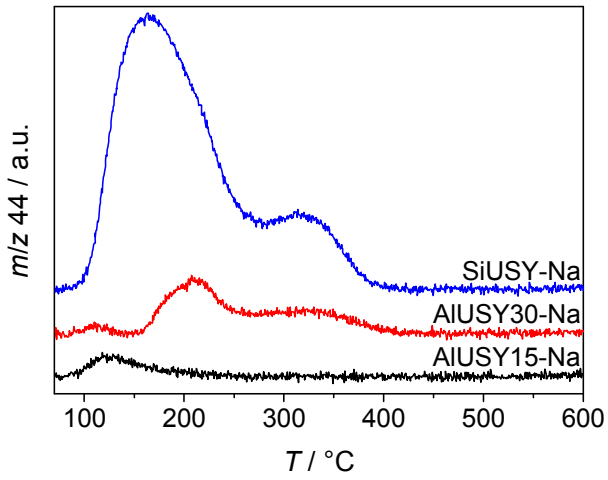

Figure S6. CO_2-TPD profiles of the USY zeolites with different aluminum content after NaOH treatment (0.1 M) in methanol.

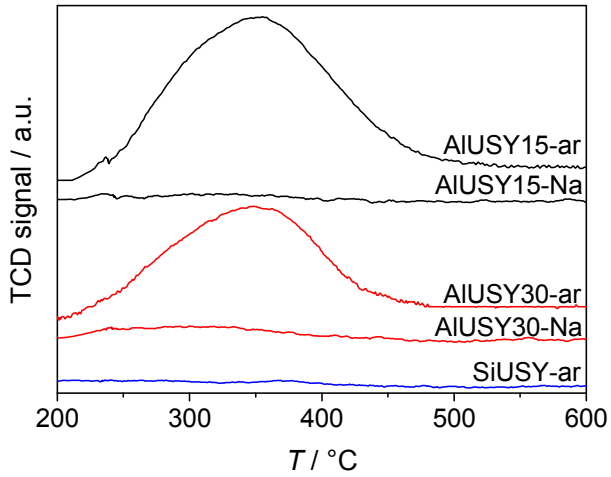

Figure S7. NH_3-TPD profiles of the as-received USY zeolites and after NaOH treatment (0.1 M) in methanol.

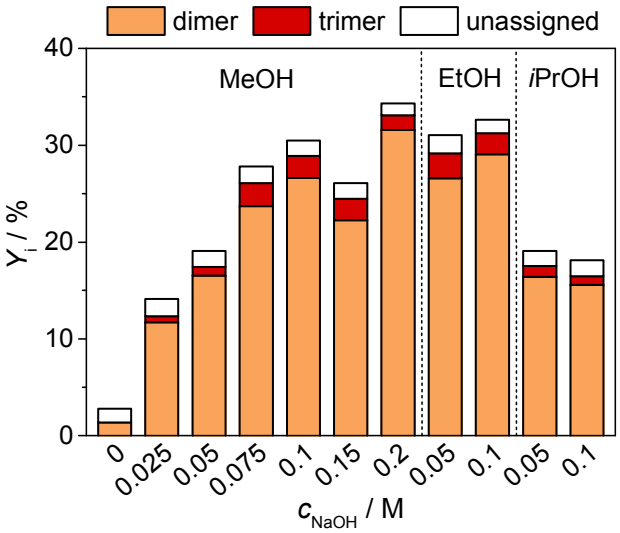

Figure S8. Product yields in the self-condensation of propanal evidenced over SiUSY zeolites alkaline treated with varying concentrations of NaOH in methanol, ethanol, and isopropanol.

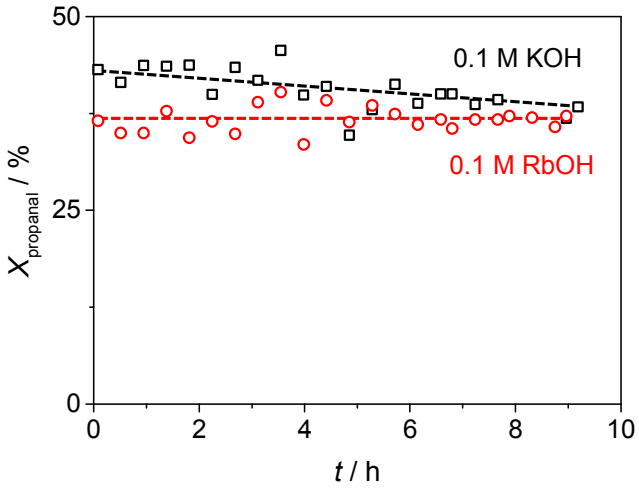

Figure S9. Propanal conversion versus time on stream over SiUSY zeolites alkaline treated with KOH or RbOH (0.1 M) in methanol.

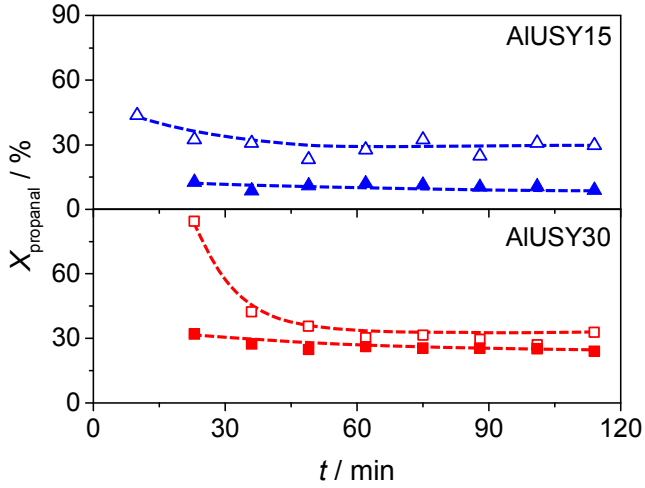

Figure S10. Propanal conversion versus time on stream over the as-received AlUSY zeolites (open symbols) and after NaOH treatment (0.1 M) in methanol (solid symbols).