From layered zeolite precursors to zeolites with a three-dimensional porosity: textural and structural modifications through alkaline treatment

Trees De Baerdemaeker [a], Mathias Feyen [b],Thomas Vanbergen [a], Ulrich Müller [b], Bilge Yilmaz [c], Feng-Shou Xiao [d], Weiping Zhang [e], Toshiyuki Yokoi [f], Xinhe Bao [g], Dirk E. De Vos [a,*] and Hermann Gies [h,*]

[a] Centre for Surface Chemistry and Catalysis, KU Leuven, 3001, Leuven, Belgium; [b] BASF SE, Chemicals Research and Engineering, 67056, Ludwigshafen, Germany; [c] BASF Corporation, Chemicals Research and Engineering, Iselin, NJ 08830, USA; [d] Zhejiang University, 310028, Hangzhou, China; [e] State Key Laboratory of Fine Chemicals, Dalian University of Technology, 116024, Dalian, China; [f] Chemical Resources Laboratory, Tokyo Institute of Technology, 226-8503, Yokohama, Japan; [g] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, 116023, Dalian, China; [h] Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum, 44780, Bochum, Germany

Supplementary information

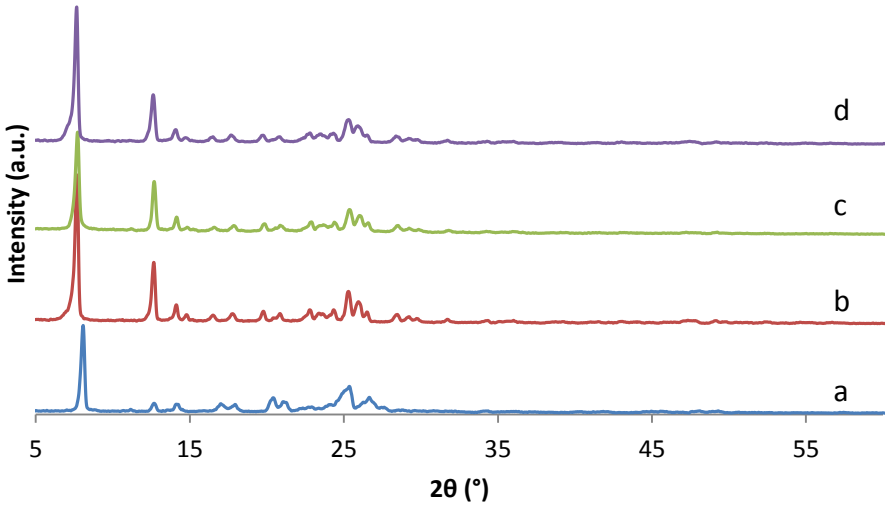

Figure S1. Powder XRD patterns of Al-RUB-36 (a) and of Al-COE-4 obtained via interlayer expansion using DCDMS and HCl (b), DEDMS and H_2SO_4 (c), and H_2SO_4 (d).

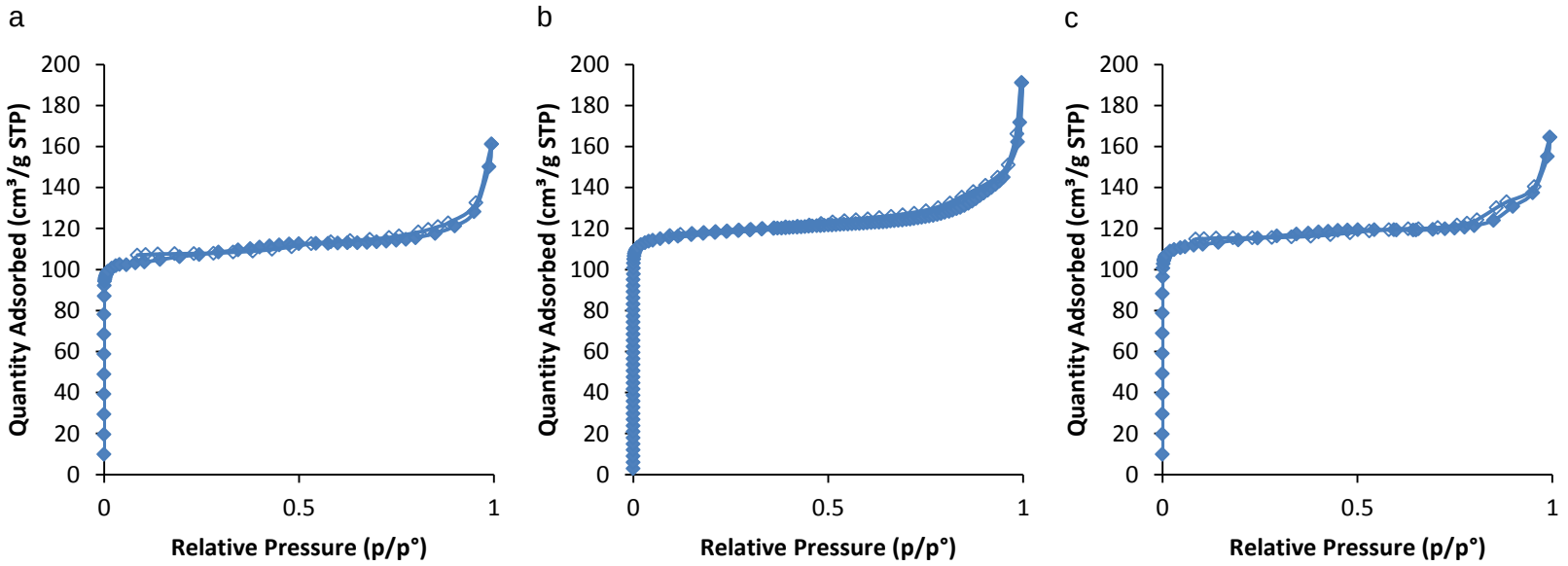

Figure S2. Nitrogen physisorption isotherms of Al-COE-4 obtained via interlayer expansion using DCDMS and HCl (a), DEDMS and H_2SO_4 (b), and H_2SO_4 (c). Filled symbols = adsorption; open symbols = desorption.

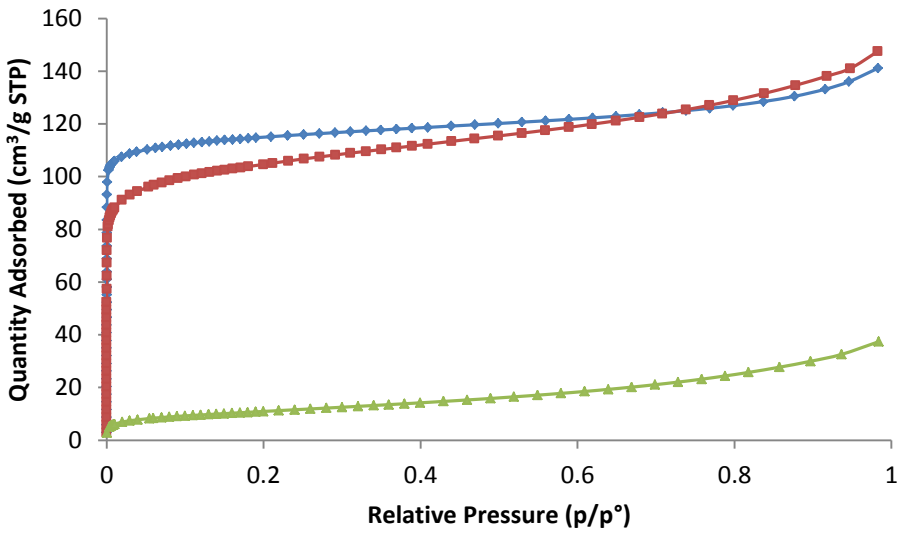

Figure S3. Ar adsorption isotherms at 77K of Al-COE-4 from DEDMS and H_2SO_4 synthesis as synthesized (blue, median pore width 6.5 Å), after alkaline treatment with 0.025 M TPAOH (red, median pore width 6.3 Å), and after alkaline treatment with 0.1 M DEDMAOH (green).

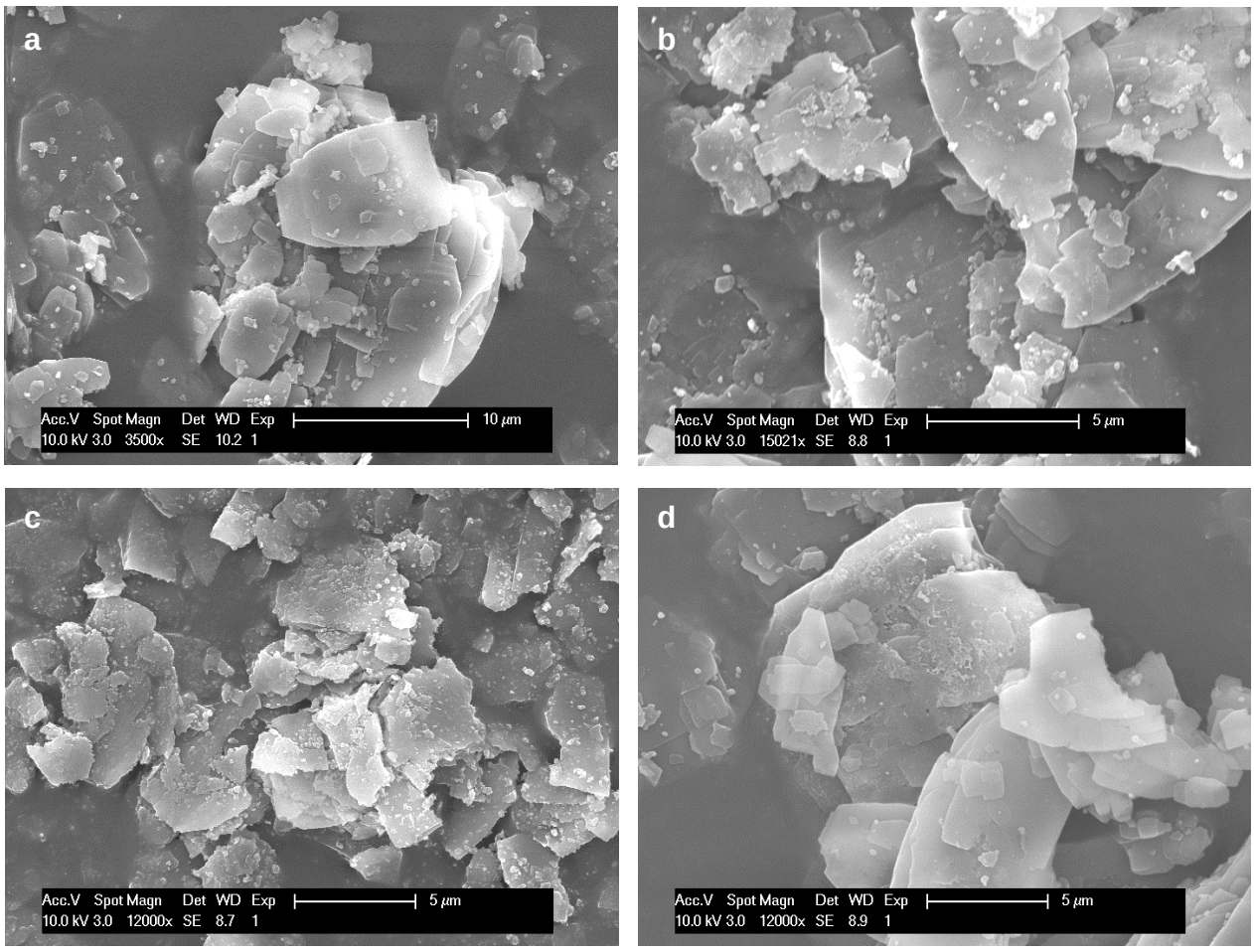

Figure S4. SEM images of Al-COE-4 from DCDMS and HCl synthesis: as synthesized (a), after treatment with 0.025M TPAOH, resulting in FER (b), after treatment with 0.1M TPAOH, resulting in FER (c), and after treatment with 0.2M TPAOH (d).

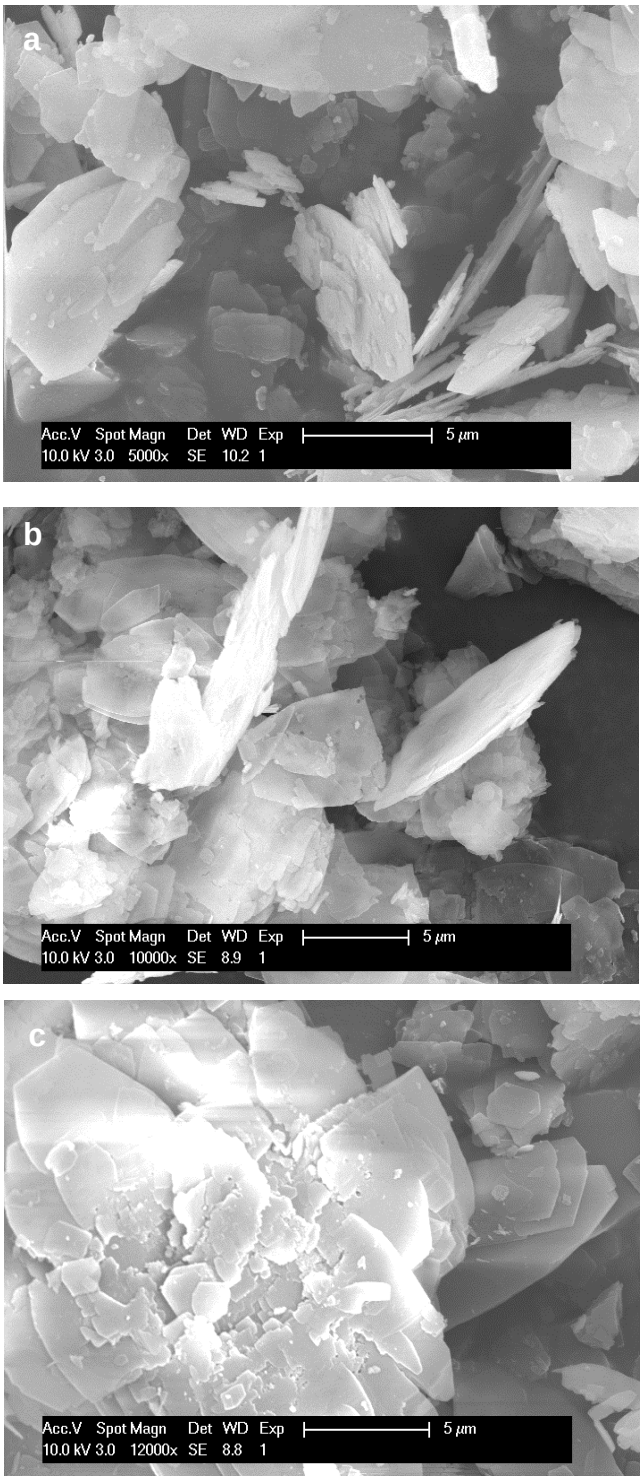

Figure S5. SEM images of Al-COE-4 from H_2SO_4 only synthesis: as synthesized (a), after treatment with 0.025M TPAOH, resulting in FER (b), and after treatment with 0.2M TPAOH (c). Note the dissolution from the crystal edges in (c).

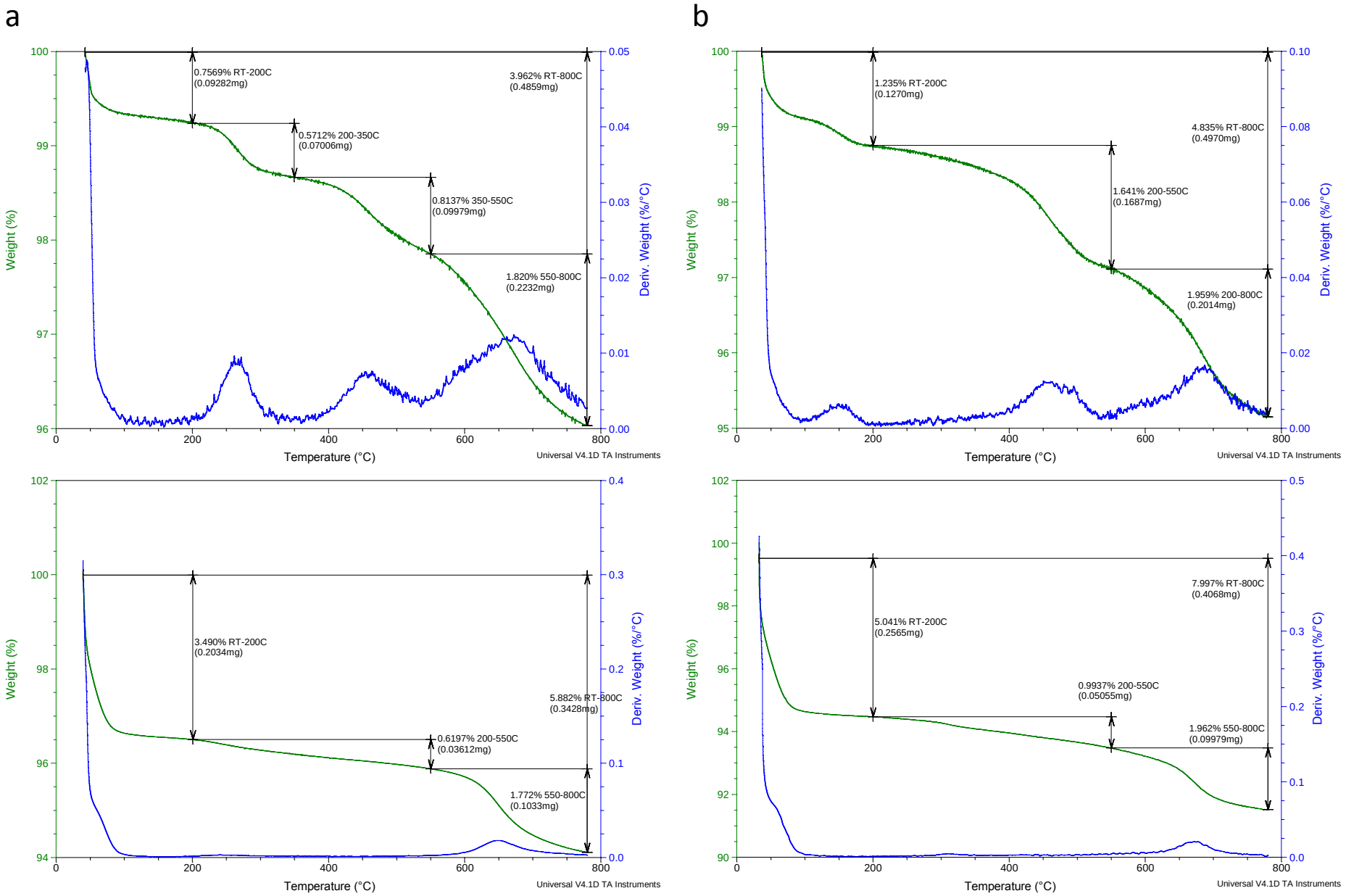

Figure S6. TG and DTG curves of Al-COE-3 (top) and Al-COE-4 (bottom) from DCDMS and HCl synthesis (a) and from H_2SO_4 only synthesis (b). Analysis was performed on hydrated samples stored under ambient conditions. (D)TG = (differential) thermogravimetry.

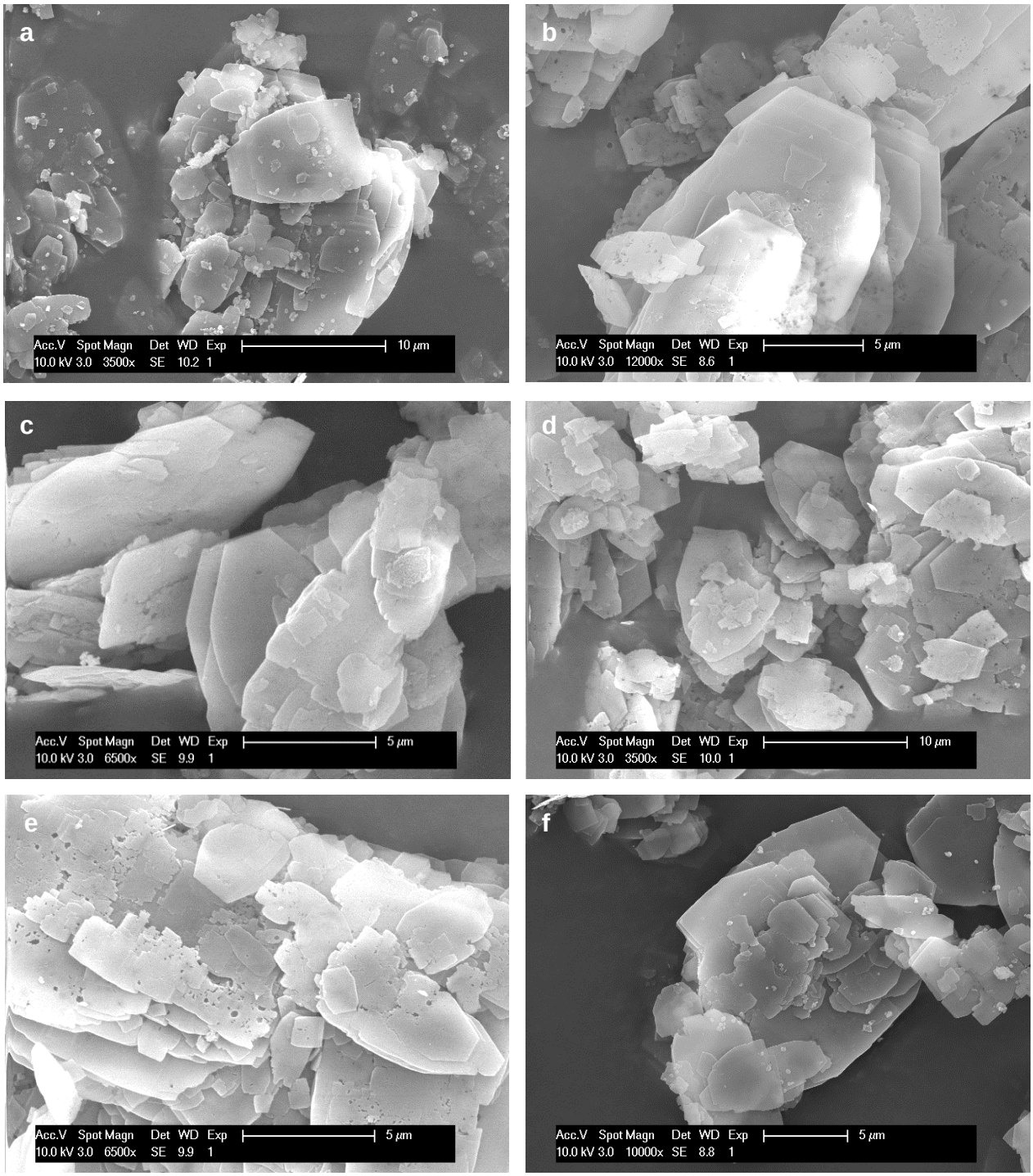

Figure S7. SEM images of Al-COE-4 from DCDMS and HCl synthesis: as synthesized (a), after treatment of the Al-COE-3 form with 0.2M NaOH (b), with 0.2M NaOH and 0.003M $Al(OH)_4^-$ (c), with 0.025M TPAOH (d), with 0.1M TPAOH (e), and with 0.2M TPAOH (f).

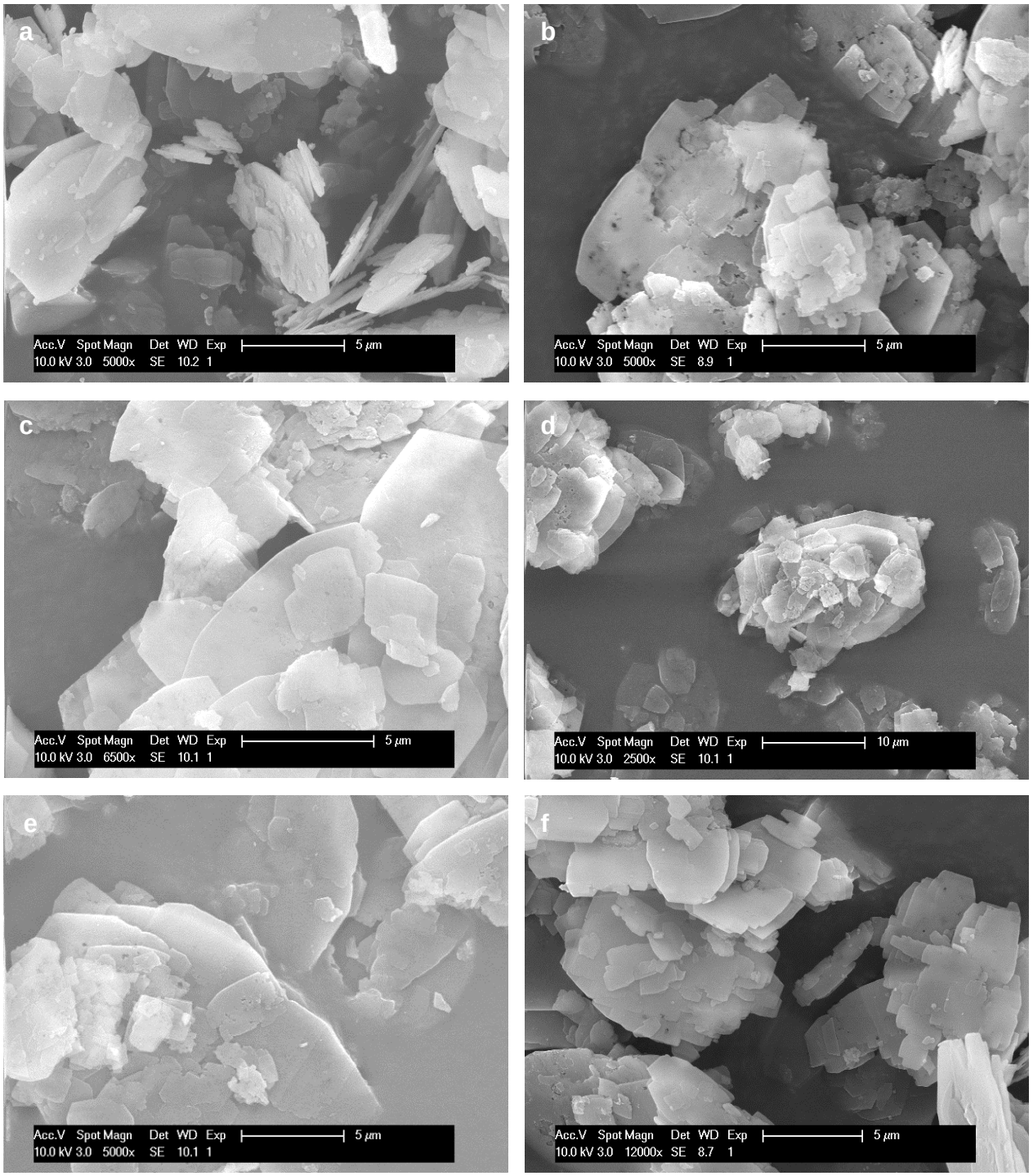

Figure S8. SEM images of Al-COE-4 from H_2SO_4 only synthesis: as synthesized (a), after treatment of the Al-COE-3 form with 0.2M NaOH (b), with 0.2M NaOH and 0.003M $Al(OH)_4^-$ (c), with 0.025M TPAOH (d), with 0.1M TPAOH (e), and with 0.2M TPAOH (f).

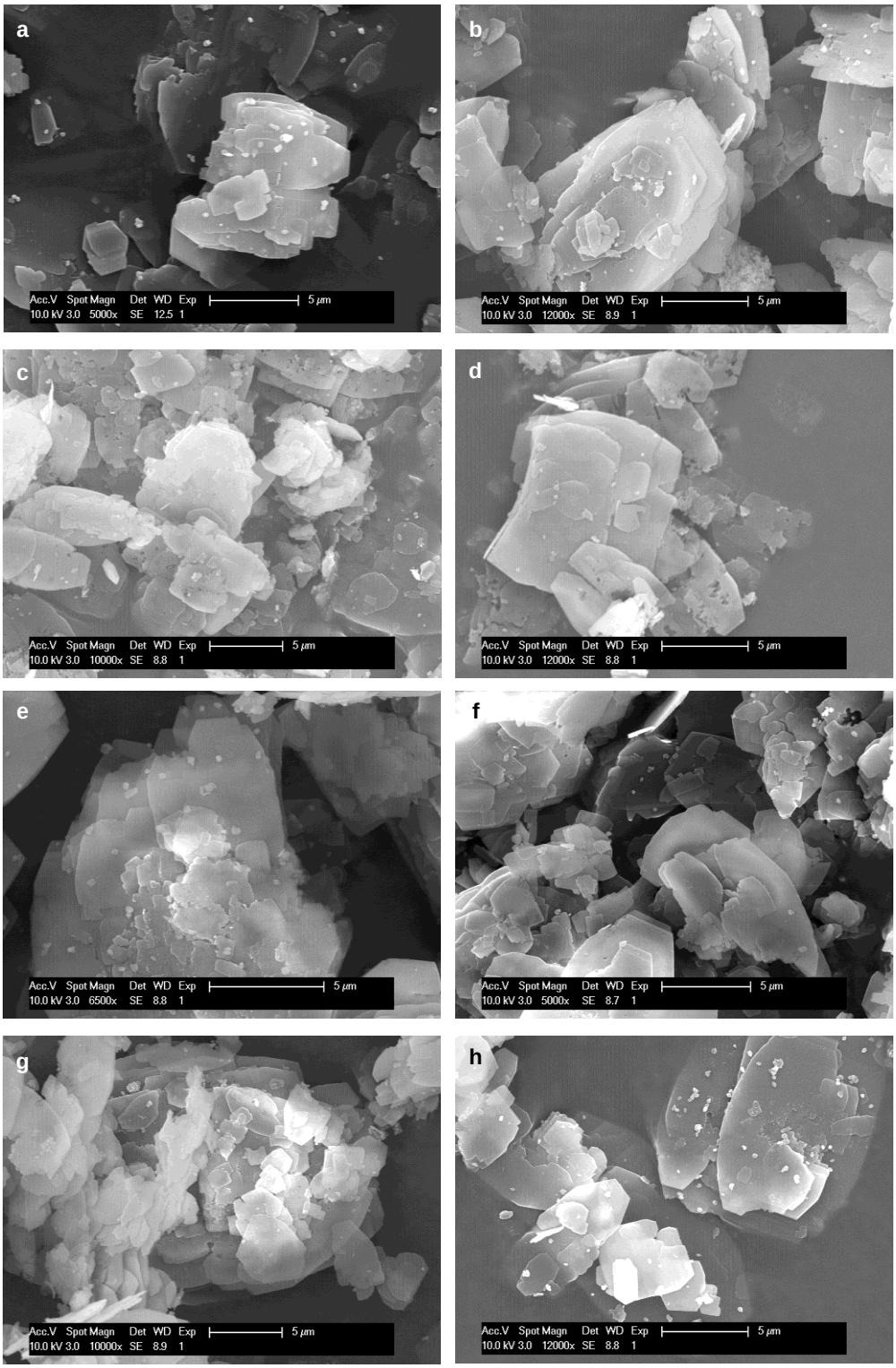

Figure S9. SEM images of Al-RUB-36 as synthesized (a), after treatment with 0.2 M NaOH (b), with 0.2 M NaOH for 2 h (c), with 0.4 M NaOH at 75 °C for 2 h (d), with 0.2 M NaOH and 0.003 M $Al(OH)_4^-$ (e), with 0.025 M TPAOH (f), with 0.1 M TPAOH (g), and with 0.2 M TPAOH (h). Images were collected after calcination.

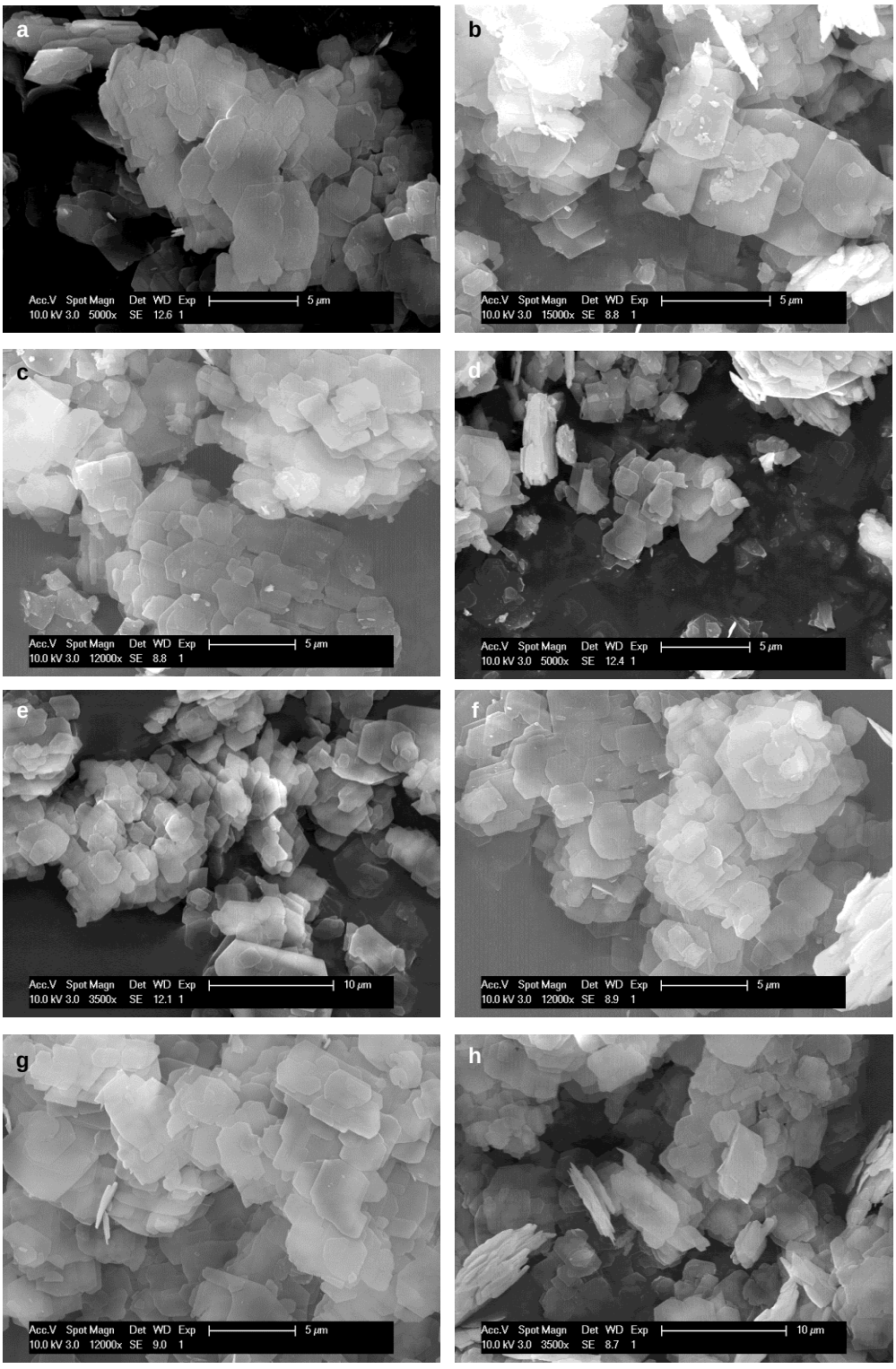

Figure S10. SEM images of RUB-36 as synthesized (a), after treatment with 0.2 M NaOH (b), with 0.2 M NaOH and 0.003 M $Al(OH)_4^-$ (c), with 0.2 M NaOH and 0.003 M $Al(OH)_4^-$ followed by interlayer expansion with DCDMs and HCl (d), with 0.2 M NaOH and 0.03 M $Al(OH)_4^-$ followed by interlayer expansion with DCDMs and HCl (e), with 0.025 M TPAOH (f), with 0.1 M TPAOH (g), and with 0.2 M TPAOH (h).

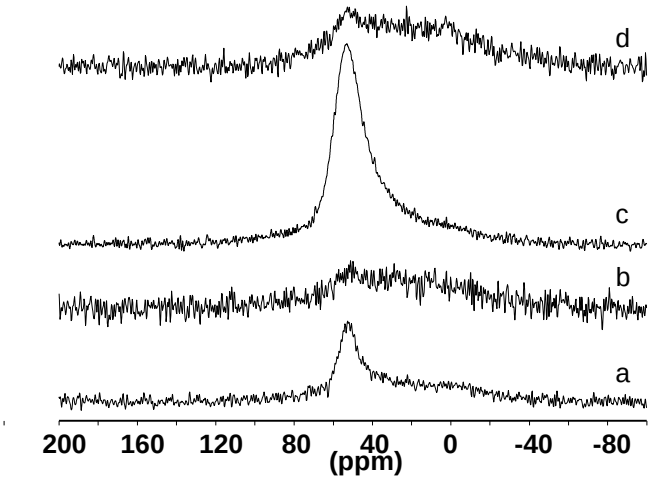

Figure S11. ^{27}Al MAS NMR spectra of RUB-36 treated with 0.2 M NaOH and 0.003 M $Al(OH)_4^-$ (a), treated with 0.2 M NaOH and 0.003M $Al(OH)_4^-$ followed by interlayer expansion with DCDMS and HCl (b), treated with 0.2 M NaOH and 0.03 M $Al(OH)_4^-$ (c), and treated with 0.2 M NaOH and 0.03 M $Al(OH)_4^-$ followed by interlayer expansion with DCDMS and HCl (d).

Table S1. Yield, composition, structure and texture of samples obtained after alkaline treatment of Al-RUB-36.

Entry	Treatment[a]	Yield (%)	Structure	Si/Al[b]	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
1	-	-	CDO	102	260	55	0.18	0.11	0.07
2	0.2 M NaOH	83	CDO	162	272	70	0.21	0.11	0.10
3[c]	0.2 M NaOH	76	CDO	158	225	40	0.19	0.10	0.09
4[c,d]	0.4 M NaOH	53	CDO	140	259	57	0.26	0.10	0.16
5	0.2 M NaOH, 0.003 M $Al(OH)_4^-$	87	CDO	86	285	56	0.22	0.12	0.10
6[e]	0.2 M NaOH, 0.003 M $Al(OH)_4^-$	87	IEZ-CDO	230	321	24	0.21	0.15	0.06
7	0.025 M TPAOH	84	CDO	182	260	55	0.18	0.11	0.07
8	0.1 M TPAOH	85	CDO	208	273	66	0.20	0.11	0.09
9	0.2 M TPAOH	95	CDO	131	272	64	0.19	0.11	0.08
10	0.2 M DEDMAOH	93	CDO	200	260	45	0.19	0.11	0.08

[a]In entries 2-8, for base concentrations between 0.2 M, NaOH was added to bring the $[OH^-]$ at 0.2 M. [b]ICP. [c]treatment duration 120 min. [d]treatment temperature 75°C. [e]The alkaline treatment was immediately followed by interlayer expansion (DCDMS, HCl procedure) and calcination into the Al-COE-4 form.

Table S2. Yield, composition, structure and texture of samples obtained after alkaline treatment of RUB-36.

Entry	Treatment[a]	Yield (%)	Structure	Si/Al[b]	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
1	-	-	CDO	-	245	37	0.21	0.10	0.11
2	0.2 M NaOH	81	CDO	-	249	49	0.23	0.10	0.13
3	0.2 M NaOH, 0.003 M $Al(OH)_4^-$	82	CDO	345	231	39	0.18	0.10	0.08
4[c]	0.2 M NaOH, 0.003 M $Al(OH)_4^-$	82	IEZ-CDO	853	349	81	0.26	0.14	0.12
5	0.2 M NaOH, 0.03 M $Al(OH)_4^-$	98	CDO	56	201	29	0.19	0.09	0.10
6[c]	0.2 M NaOH, 0.03 M $Al(OH)_4^-$	98	IEZ-CDO	-	299	35	0.24	0.14	0.10
7	0.025 M TPAOH	83	CDO	-	256	45	0.23	0.11	0.12
8	0.1 M TPAOH	83	CDO	-	244	45	0.22	0.10	0.12
9	0.2 M TPAOH	88	CDO	-	249	49	0.18	0.10	0.08

[a]In entries 2-8, for base concentrations between 0.2 M, NaOH was added to bring the $[OH^-]$ at 0.2 M. [b]ICP. [c]The alkaline treatment was immediately followed by interlayer expansion (DCDMS, HCl procedure) and calcination into the Al-COE-4 form.