Supporting Information

Structure and Phase Changes of Alumina Produced by Flame Hydrolysis

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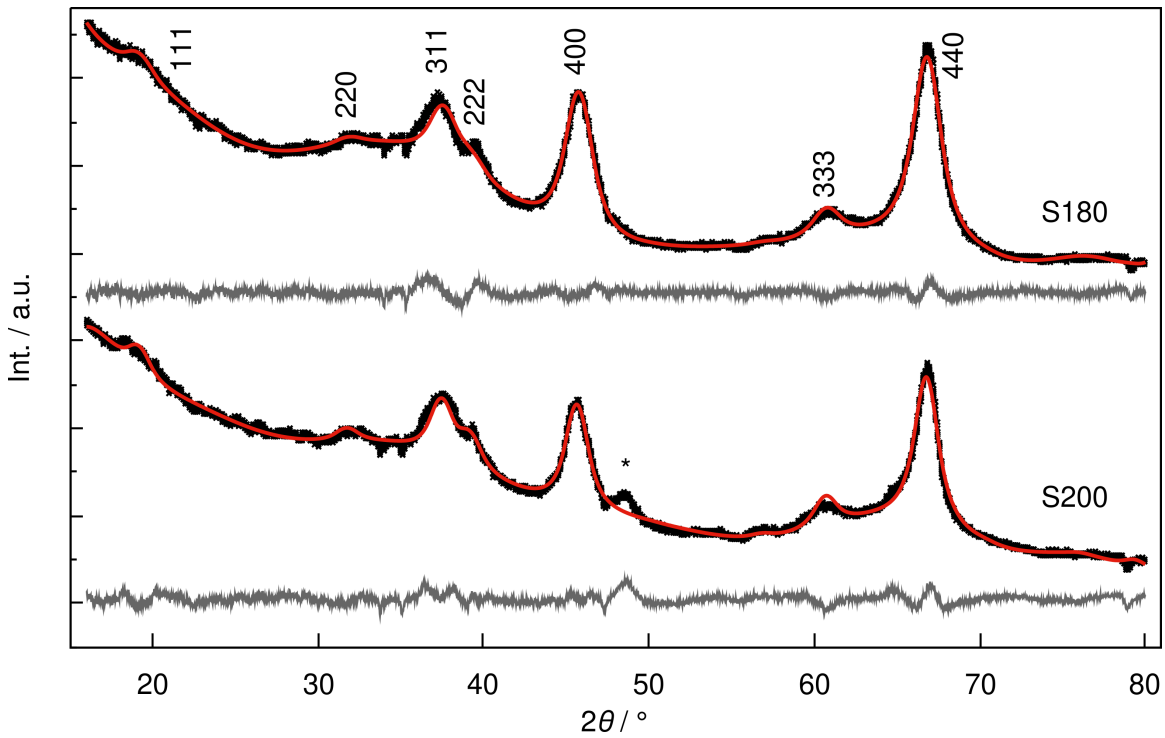

Figure S1: Rietveld refinement of the X-ray diffraction pattern for the S200 and S180 samples using Smrcok et al. spinel model for γ-alumina with a significant amount of non-spinel occupation. The black points represent the experimental data, the red solid line the calculated diffractogram with a residual profile factor R_{wp} respectively of 3.6% and 3.2%, and the grey line the difference plot. The peak marked with asterisk * is non-existent in γ-alumina.

Parameters for Rietveld refinement of γ-alumina (S220)

Table S1: Exemplary Rietveld refinement input file (used in Topas academic package[1]) with the refined parameters for the S220 sample powder diffraction (Figure 2) recorded on Guinier camera.

```
r_wp  3.02719
r_exp  2.61441499
r_p  2.25241953
gof  1.15788427
```

```
iters 100000
chi2_convergence_criteria 0.001
do_errors
```

```
xdd BET220.xy

x_calculation_step = Yobs_dx_at(Xo); convolution_step 4
bkg @  1376.83569`_1.42975713
       -1071.80372`_1.87856674
       189.442678`_1.8611632
       -4.44479503`_1.74830992
       -136.84087`_1.68499227
       -49.7694861`_1.50821558
       134.965508`_1.66444081
       12.9518863`_1.93736098
       -75.5144272`_1.49218123
       -12.6398723`_1.49710774
       15.7383351`_1.43657743
       -13.0475097`_1.29415789
       24.2915403`_1.12030175
       16.4935932`_1.31027513
LP_Factor(!th2_monochromator, 27.28)          'd8 Ge(111) monochromator Vantec Cu Ka1
CuKa1(0.0001)

Specimen_Displacement(height, 0.592872541`_42.5013868)
Specimen_Tilt(@, 1.10207389`_0.0500654427)
```

```
    Divergence( 0.823576214_0.00574586197 )
    Simple_Axial_Model(!axial, 2.15331558_0.00498608309)
    Tube_Tails(, 0.00487350562,, -0.0388314018,, 0.00329872058_LIMIT_MIN_1e-05,,
0.0620669557)

     Rp 220
     Rs 57.3
```

```
'th2_offset

     prm a1 -1.57056476`_39.9589523
     prm a2  1.38586295`_4.13264432
     prm a3  0.644076644`_85.1791326

     th2_offset = a1 Th^2 + a2 Th^1 + a3;
```

```
     start_X 16
     finish_X 80
```

```
     Out_Yobs_Ycalc_and_Difference("S220_Yobs_Ycalc_and_Diff.txt")
     Out_X_Yobs("S220_Out_X_Yobs .txt")
```

```
str
     phase_name gamma-Al2O3
     space_group "F d -3 m Z"
     Cubic (@  7.933079`_0.263268)
     volume  499.258`_49.710

  site Al1  x = 0.125;  y = 0.125;  z = 0.125;  occ Al+3  @  0.42634`_0.00754   beq 0.489532378
  site Al2  x = 0.5;      y = 0.5;      z = 0.5;      occ Al+3  @  0.60394`_0.00511   beq 0.726402884
  site O1   x = 0.25673;   y = 0.25673;   z = 0.25673;    occ O-2 1                    beq 0.876420871
  site Al3   x = 0.0;    y = 0.0;     z = 0.0;      occ Al+3   @  0.24762`_0.00435    beq 0.710611517
  site Al4   x = -0.123;  y = 0.125;  z = 0.125;   occ Al+3   @  0.08999`_0.00264 beq 0.473741011

     LVol_FWHM_CS_G_L(1, 5.19609424`_0.422947564, 0.89, 7.26466565`_0.581104289,  ,  ,
cslc, 8.16254567`_0.652926168)
     e0_from_Strain( 2.18048578e-07`_0.000379272174, , , slc, 0.0001`_0.173939301) 'eo single
strain value from Gaussian / Lorentzian
```

```
scale @  0.00120704504`_1.678e-05
r_bragg  0.205480314
Phase_Density_g_on_cm3( 3.61930318`_0.360609447)
```

Spectral Simulations of ^{27}Al MAS NMR Spectra

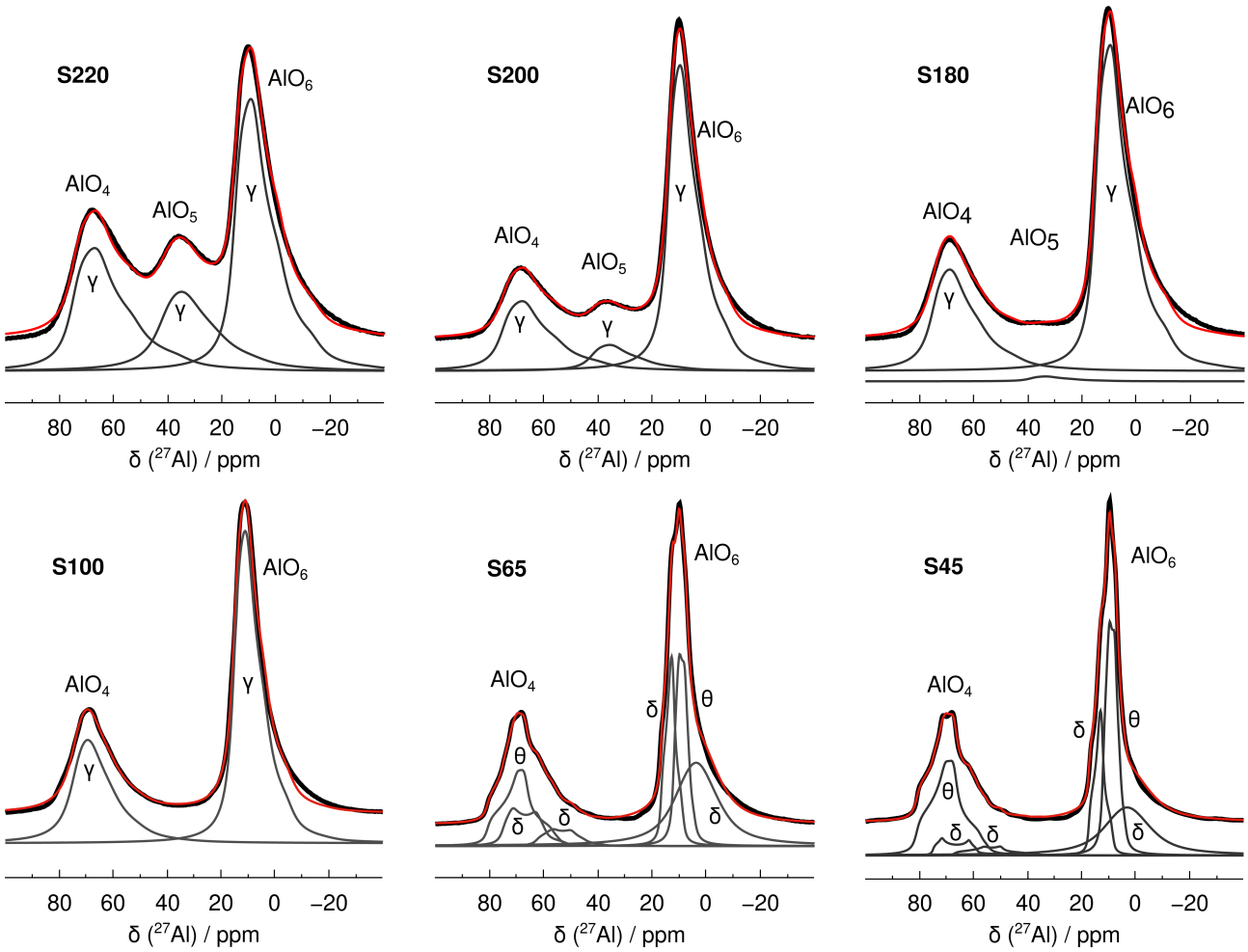

Figure S2: ^{27}Al MAS NMR spectra simulated using Czjzek model for S220 to S100 samples, using Q mas 1/2 model for the S65–45 samples as implemented in DMfit software.[1] The experimental data are shown in black, the total simulated spectra in red, and the individual decomposed spectra in grey.

Spectral Parameters Determined by Simulations Using DMfit Software

Table S2: ^{27}Al MAS NMR parameters for the AlO_4, AlO_5 and AlO_6 sites in fumed alumina materials obtained by using Dmfit package and the corresponding literature values.

BET / m^2/g	**Main phase**	**Site**	**δ_{iso} / ppm**	**C_Q / MHz**	**η**	**Model used**	**Relative intensities**	**Comment**
	γ-alumina	AlO_4	77.5 ± 0.2	3.5 ± 0.1		Czjzek	10%	[2] DNP NMR
		AlO_5	37.2 ± 0.2	4.5 ± 0.1			13%	
		AlO_6	14.0 ± 0.2	4.3 ± 0.1			78%	
	δ-alumina	AlO_4	73.2	4.6	0.6		19.6%	[3] Al isopropoxide precursor; sol-gel
		AlO_4	68.3	6.6	0.4		20.7%	
		AlO_6	16.3	4.8	0.0		25.8%	
		AlO_6	14.5	4.3	0.6		33.9%	
	θ-alumina	AlO_4	80 (1)	6.4 (0.1)	0.65(0.02)		47.8%	[4] Al tributoxide precursor; sol-gel
		AlO_6	10.5 (1)	3.5 (0.3)	0(0.1)		52.2%	
S220	γ-alumina	AlO_4	75	6.6		Czjzek	30.1%	This study
		AlO_5	42	6.2			21.5%	
		AlO_6	15.3	5.6			48.4%	
S200	γ-alumina	AlO_4	75.2	6.3		Czjzek	24.5%	This study
		AlO_5	42.2	6			8.6%	
		AlO_6	14	4.9			66.9%	
S180	γ-alumina	AlO_4	75	5.8		Czjzek	28.8%	This study
		AlO_5	39	5.5			1.2%	
		AlO_6	15	5.4			70%	
S130	γ-alumina	AlO_4	74.4	5.4		Czjzek	31%	This study
		AlO_6	15	5.1			69%	
S100		AlO_4	74.4	5.1		Czjzek	33%	This study
		AlO_6	15.0	4.7			66.7%	
S65	θ-alumina	AlO_4	80.9	6.3	0.8	Q mas	17.9%	This study

		AlO_6	12.3	3.6	0.4	1/2	19%	
	δ-alumina	AlO_4	77	6.3	0.3		9.5%	
		AlO_4	64	6.3	0.4		4.5%	
		AlO_6	16.6	3.5	0.8		16.2%	
		AlO_6	11.1	5	0.7		32.8%	
S45	θ-alumina	AlO_4	81.3	6.3	0.8	Q mas 1/2	27%	This study
		AlO_6	12.4	3.7	0.5		27.3%	
	δ-alumina	AlO_4	77.4	6.6	0.2		4.1%	
		AlO_4	67.6	7.1	0.6		3%	
		AlO_6	17.3	3.6	0.8		14%	
		AlO_6	10.8	5	0.9		24.7%	
S30	θ-alumina	AlO_4	80.4	6.1	0.9	Q mas 1/2	15.6%	This study
		AlO_6	12.7	3.9	0.5		18.3%	
	δ-alumina	AlO_4	76.6	6.4	0.2		8%	
		AlO_4	73.3	8.3	0.7		9%	
		AlO_6	16.4	3.3	1		24.1%	
		AlO_6	10.2	5.2	0.7		25%	

^{27}Al MQMAS Spectra of Fumed Alumina for the S220–45 Samples

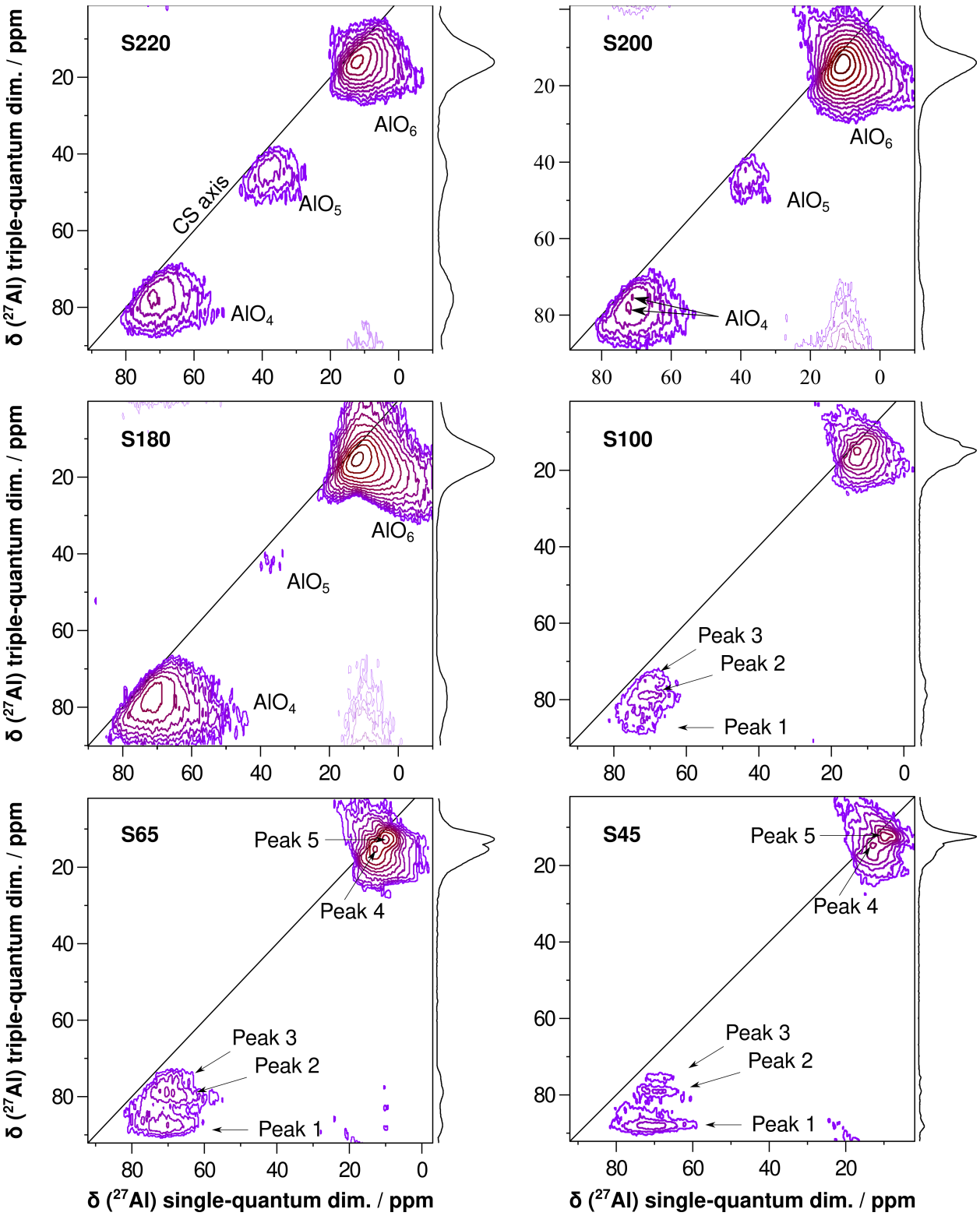

Figure S3: Sheared ^{27}Al triple-quantum MQMAS NMR spectra of fumed alumina for the S220 to S45 samples measured at 20 kHz MAS frequency. The sum projection of the isotropic spectra are shown on the right of each 2D spectrum.

Projections of ^{27}Al MQMAS Spectra of Fumed Alumina for the S220–45 Samples

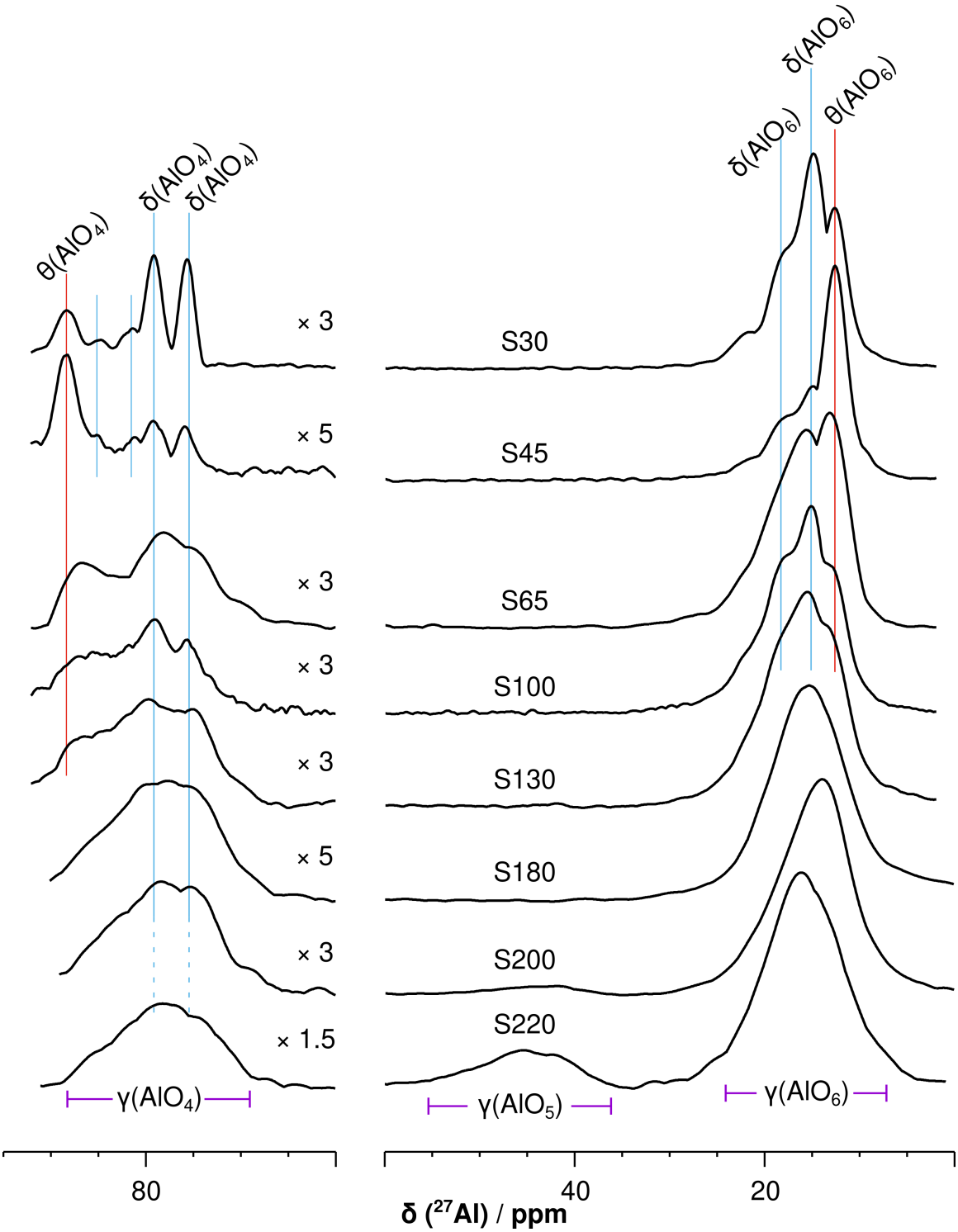

Figure S4: Sum projections of ^{27}Al triple-quantum MQMAS spectra of fumed alumina samples with S220–30 measured at 20 kHz MAS frequency. In the shearing execution, not all the 2D spectra are shifted by the same value.

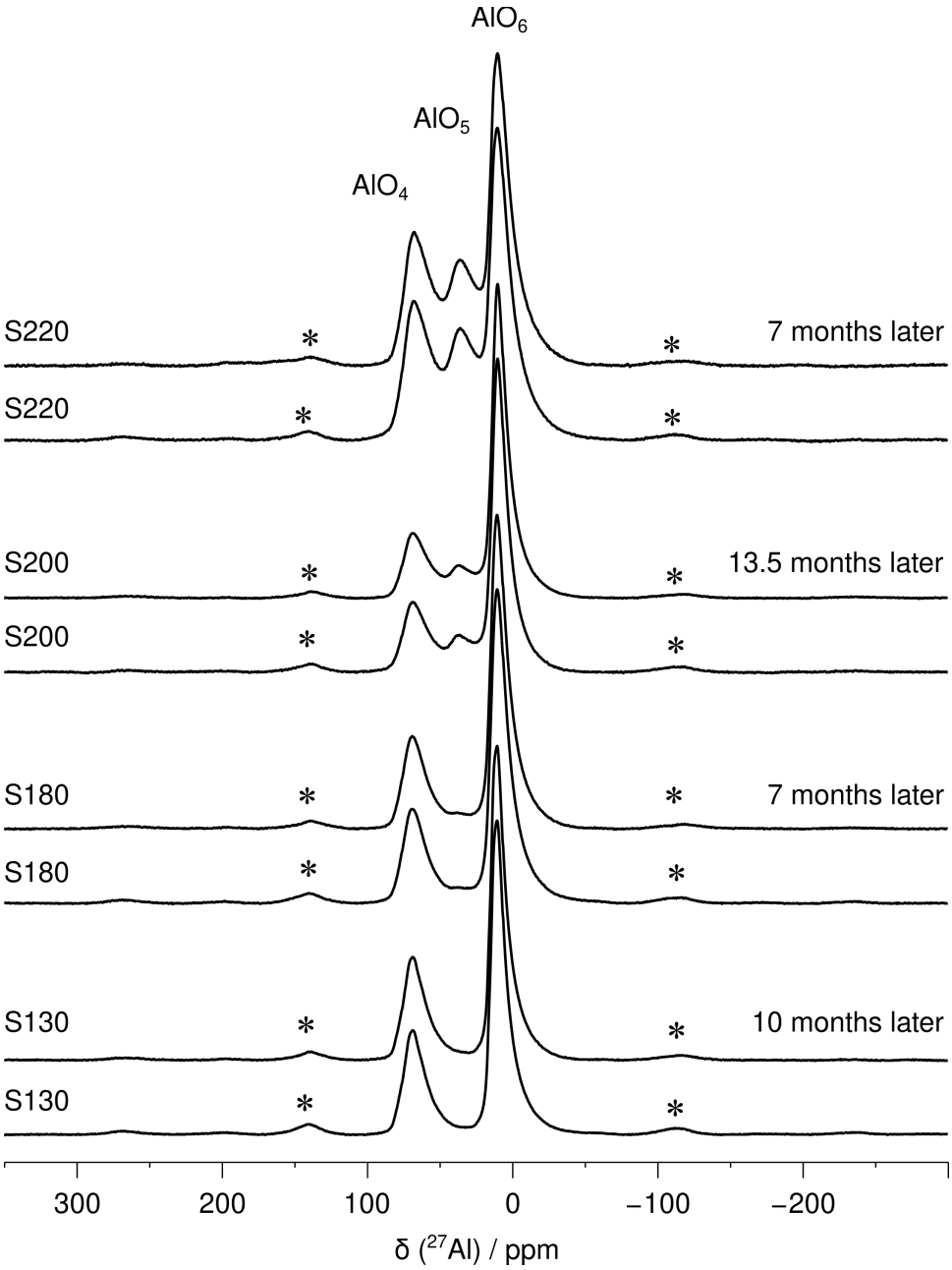

Figure S5: ^{27}Al MAS NMR spectra intended to reveal an aging effect on the samples S220 to S130 measured at 20 kHz MAS frequency a second time after various periods of time. As is obvious, there is no noticeable change in the shape or intensities of the spectra.

TEM Images of Fumed Alumina for the S220 to S30 Samples

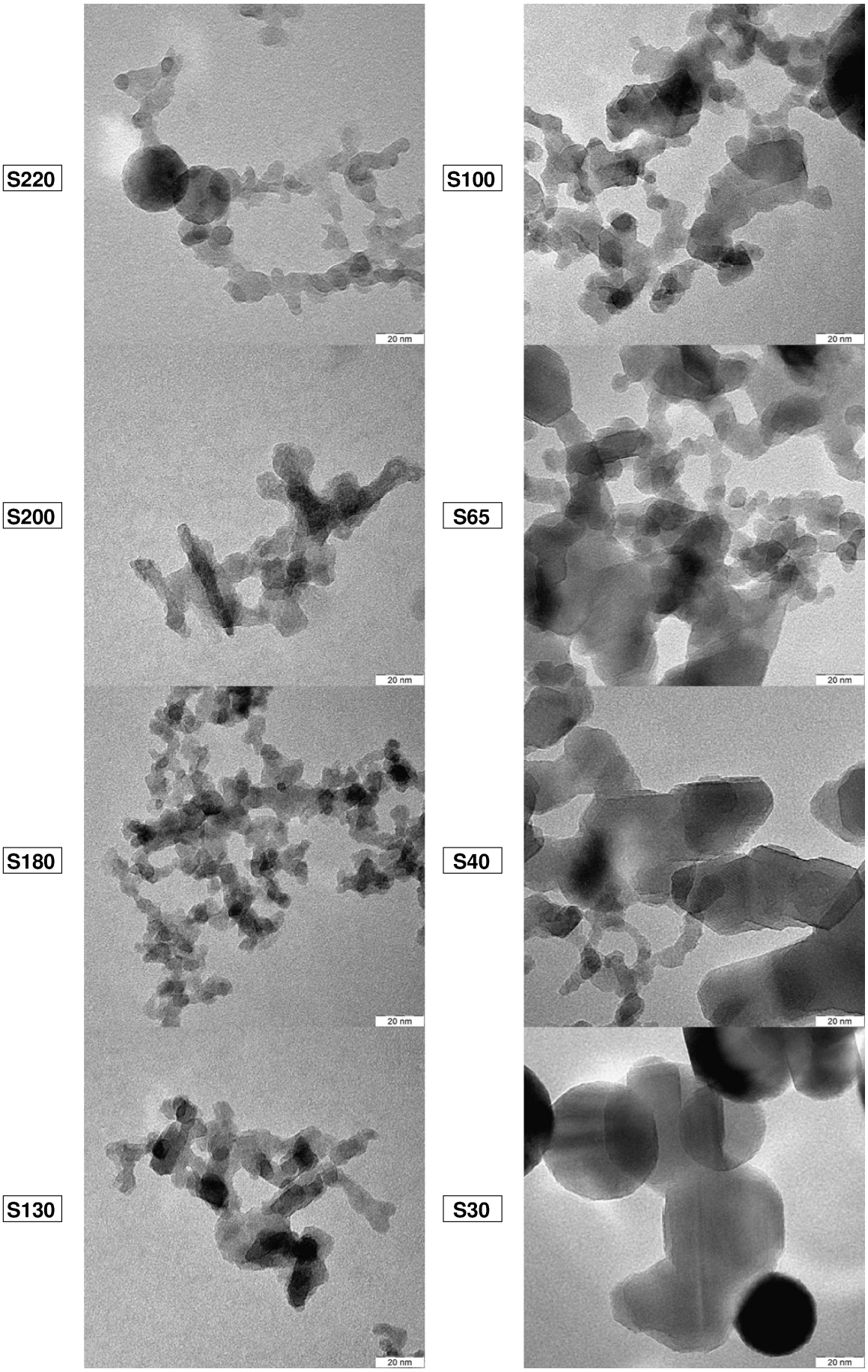

Figure S6: TEM images of fumed alumina samples S220 to S30 samples.

Histograms for Particles Sizes for the S220 to S30 Samples

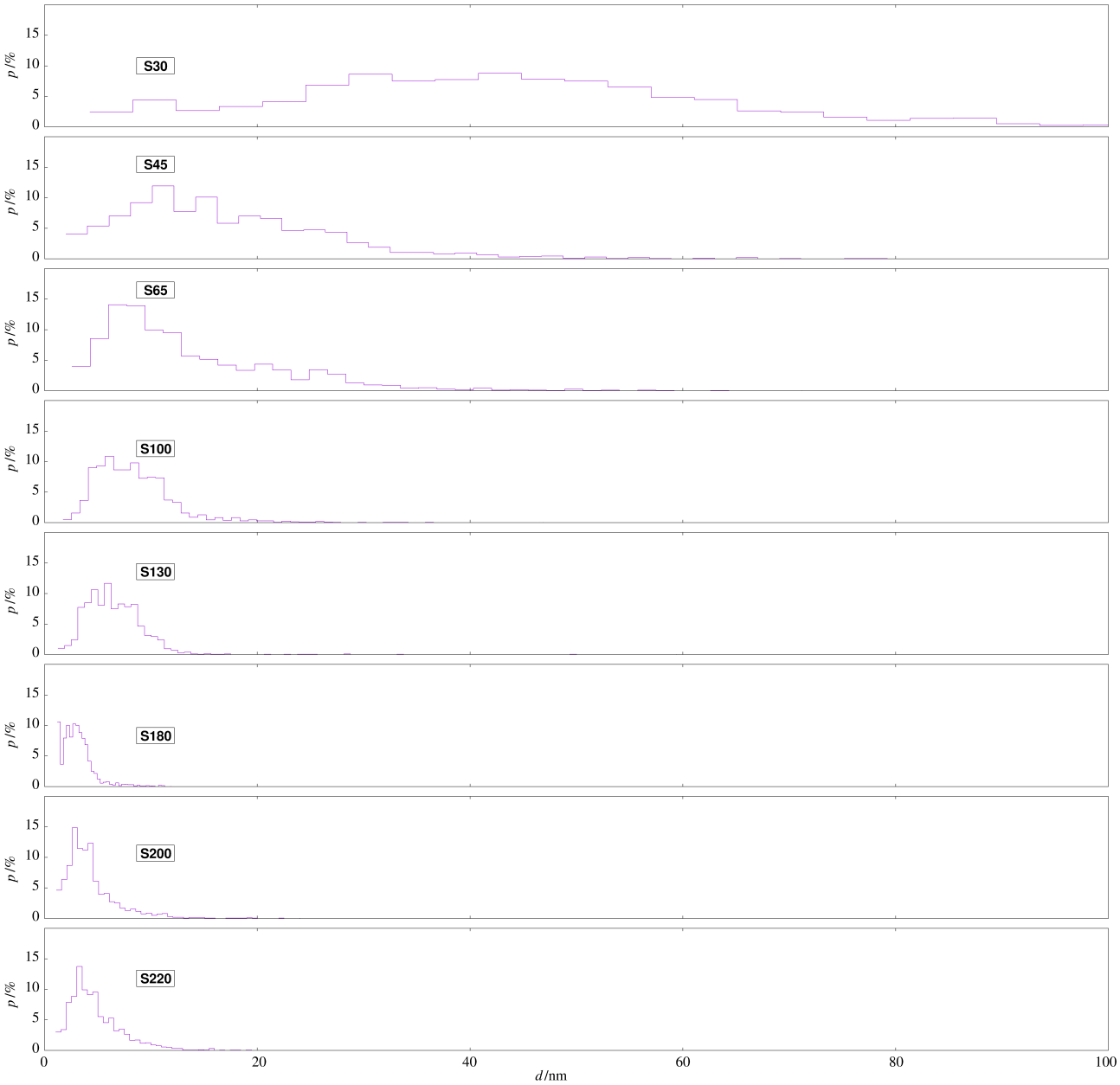

Figure S7: Particle size distribution of the fumed alumina samples S220 to S30 obtained by analysis of TEM micrographs of about 2000 particles each. For agglomerates the primary particles were counted.

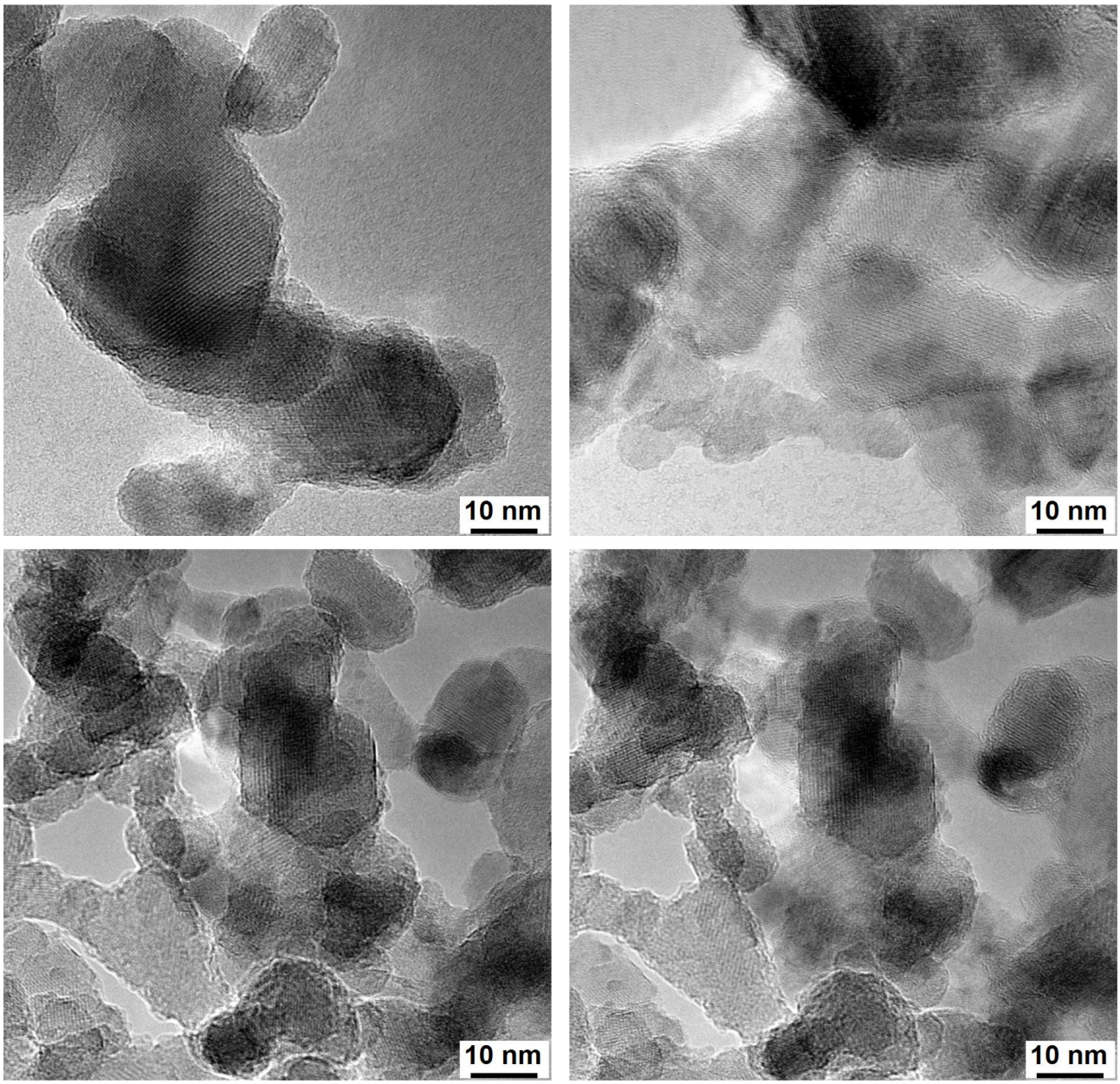

Figure S8: High-resolution TEM pictures of fumed alumina S65. The picture sure primary particles of different sizes which are the result of nucleation (small monocrystalline particles), collision and coalescence (bigger monocrystalline particles) and agglomeration and aggregation (bigger polycrystalline particles.

References

[1] A.A. Coelho, J. Appl. Cryst. 51 (2018) 210–218.
[2] M. Mais, S. Paul, N.S. Barrow, J.J. Titman, Johnson Matthey Technol. Rev. 62 (2018) 271–278.
[3] S. Xu, N.R. Jaegers, W. Hu, J.H. Kwak, X. Bao, J. Sun, Y. Wang, J.Z. Hu, ACS Omega 6 (2021) 4090–4099.
[4] L.A. O'Dell, S.L.P. Savin, A.V. Chadwick, M.E. Smith, Solid State Nucl. Magn. Reson. 31 (2007) 169–173.