

# Generation of mesoporosity in H-Y zeolites by basic or acid/basic treatments: towards a guideline of optimal Si/Al ratio and basic reagent

Y. Han, K. Larmier, M. Rivallan, G. D. Pirngruber\*

IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

## Supplementary Information

**Table SI 1** **Table SI 2.**  $\text{NH}_4^+$  content in zeolite

Zeolite	Nitrogen/zeolite (wt %) <sup>a</sup>	$\text{NH}_4^+/\text{Al}^{\text{IV}}$ (mol %) <sup>b</sup>
CBV600	0.015%	1%
CBV712	0.40%	27%
CBV720	0.25%	25%
CBV760	0.027%	5%

<sup>a</sup> The nitrogen content in gram in 1g of zeolite was measured by CNSH elemental analysis

<sup>b</sup> The quantity of  $\text{Al}^{\text{IV}}$  was calculated from FX and  $^{27}\text{Al}$  MAS NMR results

**CNHS elemental analysis.** Nitrogen content in weight percentage in zeolite was measured by CNHS elemental analysis. The analysis was carried out using a “FlashSmar” of Thermofisher. The sample was placed in a tin boat and introduced into an oven in the presence of oxygen. The general process is as follows: The temperature is raised to around 1800 °C in an instant by a flash. The nitrogen is oxidized in the form of nitrogen oxides and then reduced to the state of molecular nitrogen by passage over heated copper. The gas mixture then passes through a chromatography column, which allows to separate the gaseous products obtained during combustion. Finally, the separated gases flow through a katharometer (thermal conductivity detector). It consists of two platinum wires through which a constant current flows. One of these wires is swept by the carrier gas alone (Helium: reference), the second by the carrier gas and the solutes eluted at the column outlet. These two platinum wires are integrated into two branches of a Wheatstone bridge. At the elution of each compound, the

thermal conductivity of the platinum wire changes, causing the chromatographic signal. The signal obtained is related to the quantity of elements, N, C, H and Sn present in the zeolite to be analyzed by an external calibration. Each sample was analyzed twice, and the repeatability was checked.

**Table SI 2.** Concentration of oxalic acid used

Oxalic acid/Al in zeolite (mol/mol)	M (mol L <sup>-1</sup> )
0.83	0.066
1	0.079
1.125	0.089
1.25	0.099
1.375	0.109
1.5	0.119
1.625	0.128

**Table SI 3.** pH change, loss of elements, Si/Al ratio, relative crystallinity, and UCS.

Sample	pH <sub>i</sub>	pH <sub>f</sub>	Al loss <sup>a</sup>	Si loss <sup>a</sup>	Yield (%)	Si/Al Bulk (mol/mol) <sup>b</sup>	Relative crystallinity <sup>c</sup>	UCS <sup>c</sup>	Change in the UCS <sup>d</sup>
CBV760	-	-	-	-	-	28.1	100%	24.25	-
760-TMAOH	13.3	11.36	3%	37%	47%	18.6	0%	n.d	n.d
760-TEAOH	13.44	12.2	4%	38%	38%	16.6	58%	24.163	-0.36%
760-TPAOH	13.31	12.46	4%	34%	48%	21.2	92%	24.26	0.04%
760-TBAOH	13.3	12.8	5%	28%	36%	18.5	100%	24.281	0.13%
CBV720	-	-	-	-	-	15.8	100%	24.293	-
720-TMAOH	13.5	12.8	2%	25%	50%	10.6	67%	24.265	-0.12%
720-TEAOH	13.56	13.17	3%	18%	64%	12.4	94%	24.298	0.02%
720-TPAOH	13.42	13.34	4%	11%	68%	13.9	107%	24.309	0.07%
720-TBAOH	n.m	n.m	6%	10%	72%	14.5	107%	24.305	0.05%
CBV712	-	-	-	-	-	5.8	100%	24.337	-
712-TMAOH	13.34	13.3	n.m	n.m	76%	6.6	95%	24.332	-0.02%
712-TPAOH	13.37	13.3	12.6%	4.2%	78%	6.3	95%	24.321	-0.07%
712-ox0.83	1.65	3.54	50.6%	1.2%	78%	11.3	105%	24.317	-0.08%
712-ox1	1.36	3	56.3%	1.6%	81%	14.5	96%	24.295	-0.17%
712-ox1.125	1.3	2.7	62.3%	1.3%	78%	18.0	96%	24.280	-0.23%
712-ox1.25	1.31	2.44	70.8%	1.4%	76%	22.3	85%	24.257	-0.33%
712-ox1.375	1.24	1.97	78.3%	1.6%	73%	28.6	83%	24.230	-0.44%
712-ox1.5	1.19	1.69	81.6%	1.6%	73%	36.4	76%	24.201	-0.56%
712-ox1.625	n.m	n.m	85.3%	1.7%	n.m	37.2	77%	24.194	-0.59%
712-ox0.83-TPAOH	13.4	13.14	2.5%	9.8%	n.m	10.8	102%	24.318	-0.08%
712-ox1-TPAOH	13.4	12.97	n.m	n.m	n.m	11.7	91%	24.305	-0.13%
712-ox1.125-TPAOH	13.41	12.49	0.8%	32.2%	76%	12.4	90%	24.294	-0.18%
712-ox1.25-TPAOH	13.35	11.99	0.9%	39.2%	71%	14.4	76%	24.274	-0.26%
712-ox1.375-TPAOH	13.37	11.68	0.9%	44.2%	n.m	14.9	64%	24.239	-0.40%
712-ox1.5-TPAOH	13.3	11.51	0.9%	53.6%	46%	15.8	30%	24.212	-0.51%

712-ox1.625-TPAOH	13.37	11.56	0.8%	54.6%	47%	18.3	24%	24.175	-0.67%
712-ox1.125-TBAOH	13.42	13	0.8%	17.5%	93%	15.2	96%	24.295	-0.17%
712-ox1.25-TBAOH	13.37	12.73	0.5%	26.7%	83%	16.6	93%	24.281	-0.23%
712-ox1.375-TBAOH	13.31	12.36	0.4%	32.6%	n.m	19.2	85%	24.269	-0.28%
712-ox1.5-TBAOH	13.35	11.91	0.5%	40.4%	66%	20.6	81%	24.251	-0.35%
712-ox1.625-TBAOH	13.37	12	0.4%	40.3%	53%	21.3	77%	24.237	-0.41%

<sup>a</sup> acquired from ICP-OES and XRF result of parent material <sup>b</sup> measured by XRF <sup>c</sup> determined on XRD diffractogram: Relative crystallinity using ASTM method assuming that the crystallinity of starting material (CBV712, CBV720 and CBV760) is 100%. <sup>d</sup>100% x (UCS<sub>final</sub>-UCS<sub>initial</sub>)/UCS<sub>initial</sub> where UCS<sub>initial</sub>=UCS of starting material (CBV712, CBV720 and CBV760)

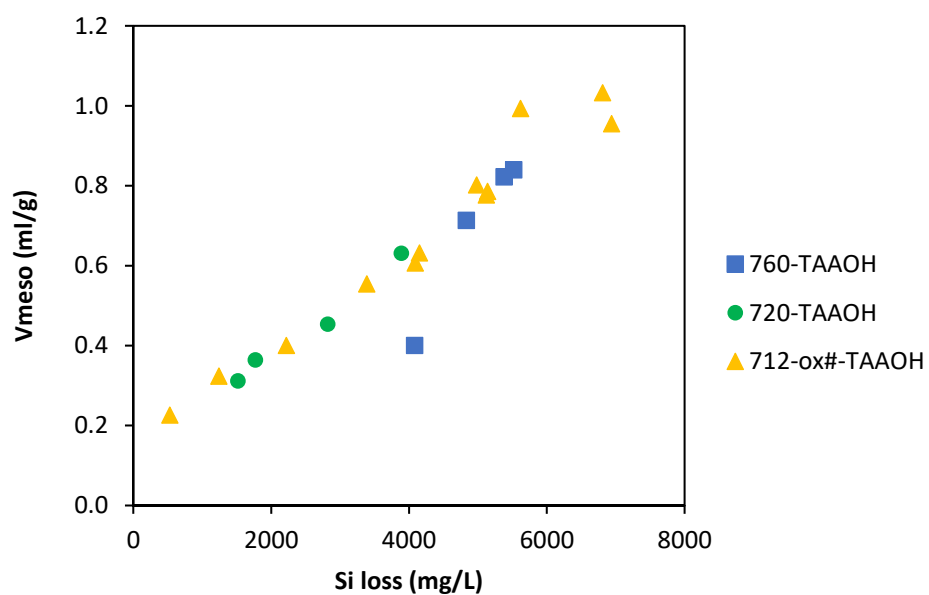
\* n.m: not measured; n.d: not determined

**Equation SI 4.** Calculation of (a) OH<sup>-</sup> consumed during base treatment and (b) H<sup>+</sup> consumed during acid treatment.

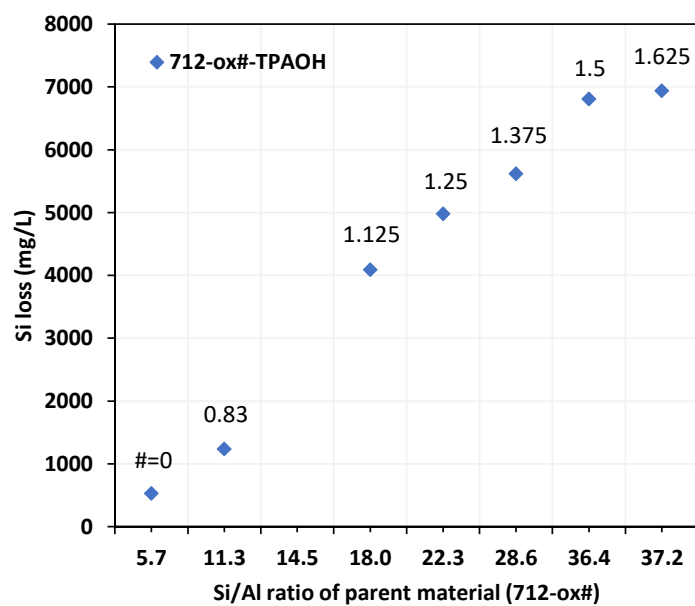
$$(a) \quad OH^- \text{ consumed } (\%) = \frac{[OH^-]_{initial} - [OH^-]_{final}}{[OH^-]_{initial}} \times 100\% = \frac{10^{14-pH_i} - 10^{14-pH_f}}{10^{14-pH_i}} \times 100\%$$

$$(b) \quad H^+ \text{ consumed } (\%) = \frac{[H^+]_{initial} - [H^+]_{final}}{[H^+]_{initial}} \times 100\% = \frac{10^{-pH_i} - 10^{-pH_f}}{10^{-pH_i}} \times 100\%$$

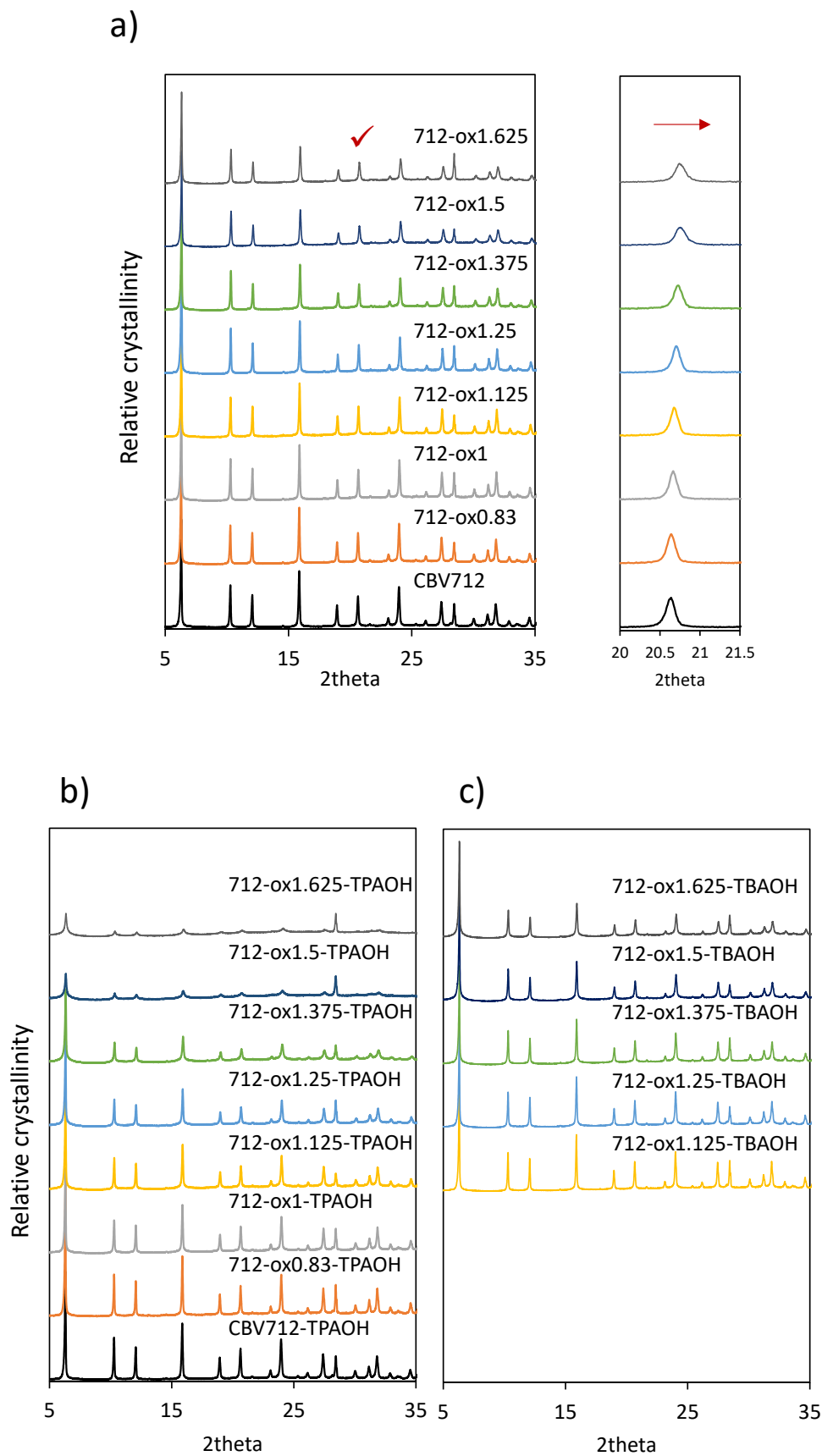
a)



b)



**Figure SI 5.** a) Relationship between Si loss and mesopore volume of desilicated samples and (b) between Si loss and Si/Al ratio of parent material of modified 712 samples

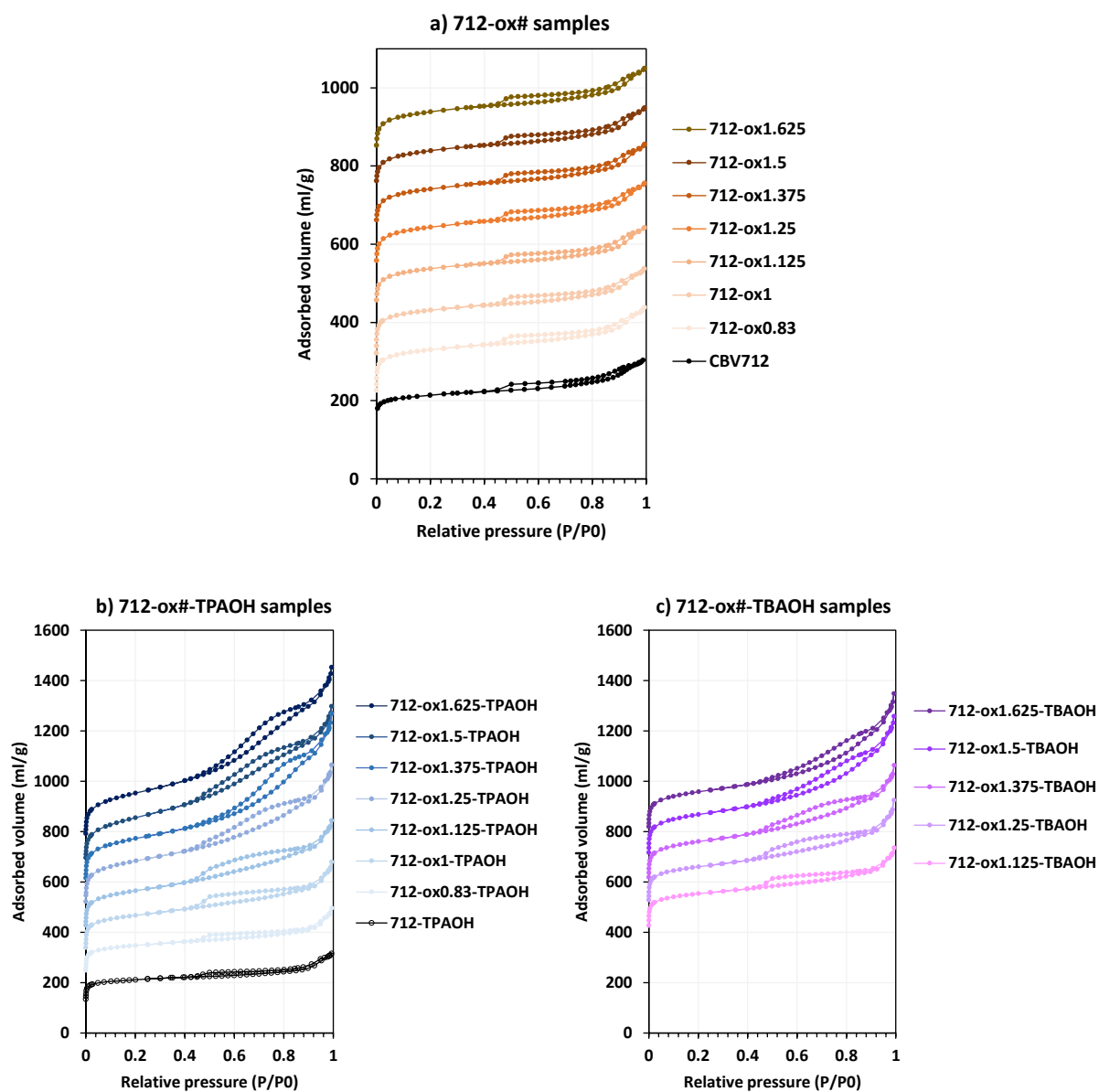


**Figure SI 6.** XRD diffractogram of 712-ox# (a), 712-ox#-TPAOH (b) and 712-ox#-TBAOH (c)

**Table SI 7.** Porosity of parent and modified CBV760, CBV720 and CBV712

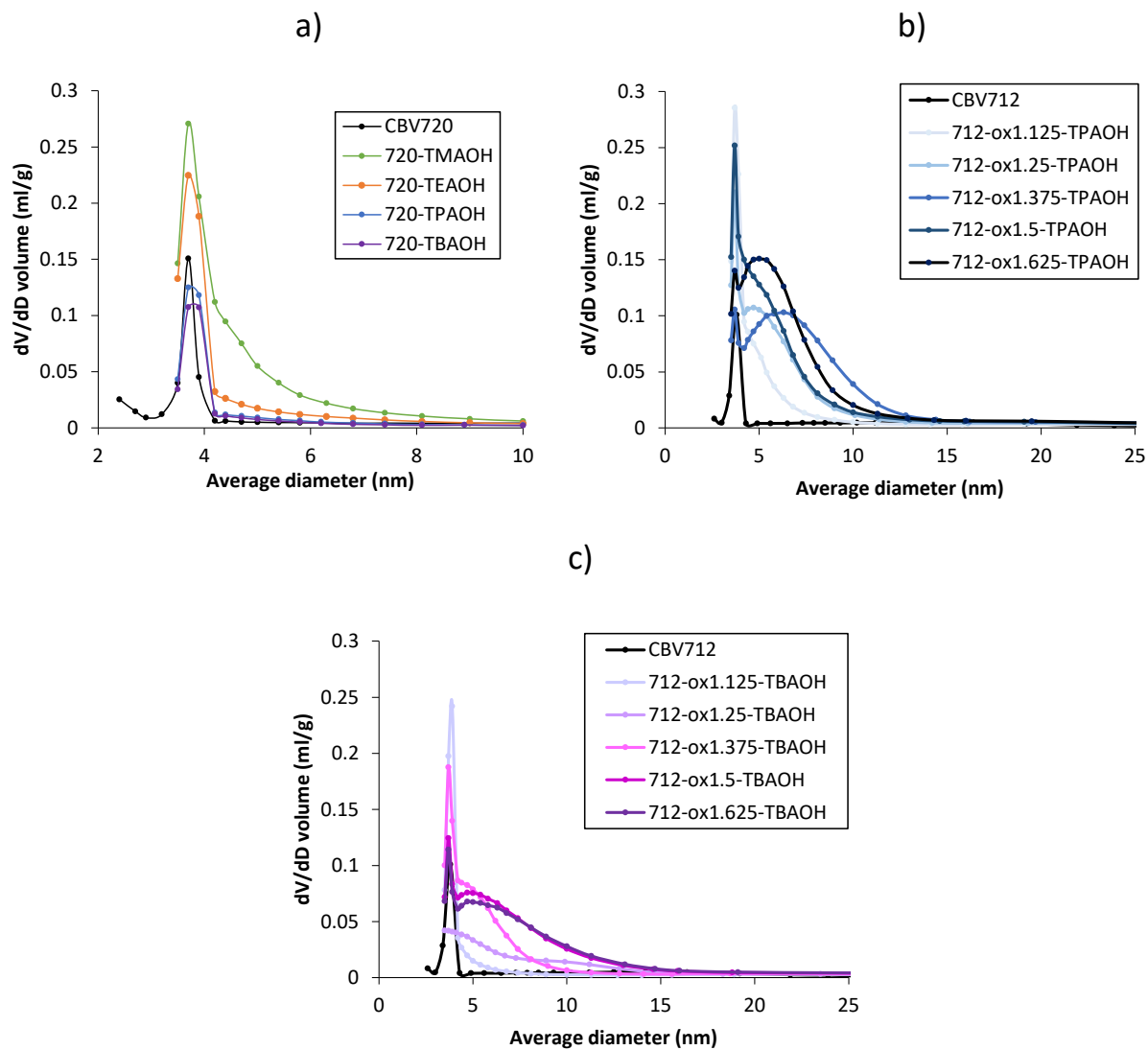
Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$S_{\text{meso}}^{\text{a}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{micro}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{meso}}^{\text{b}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{total}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{BJH}}$ adsorption ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\text{BJH}}$ desorption ( $\text{cm}^3 \text{g}^{-1}$ )
CBV760	859	272	0.251	0.322	0.573	0.211	0.251
760-TMAOH	549	515	0.053	0.822	0.875	0.705	0.751
760-TEAOH	827	446	0.18	0.839	1.019	0.756	0.803
760-TPAOH	895	378	0.224	0.713	0.936	0.615	0.666
760-TBAOH	882	274	0.249	0.4	0.650	0.311	0.353
CBV720	885	256	0.251	0.277	0.528	0.174	0.208
720-TMAOH	829	422	0.184	0.631	0.815	0.498	0.544
720-TEAOH	834	281	0.228	0.453	0.681	0.358	0.393
720-TPAOH	903	252	0.261	0.364	0.625	0.262	0.284
720-TBAOH	904	229	0.268	0.311	0.579	0.221	0.241
CBV712	845	147	0.267	0.202	0.469	0.159	0.184
712-TMAOH	820	160	0.255	0.239	0.494	0.177	0.199
712-TPAOH	829	150	0.262	0.226	0.488	0.169	0.188
712-ox0.83	879	198	0.269	0.255	0.524	0.176	0.200
712-ox1	881	199	0.271	0.252	0.522	0.173	0.196
712-ox1.125	907	222	0.270	0.260	0.530	0.172	0.205
712-ox1.25	929	226	0.278	0.273	0.551	0.184	0.215
712-ox1.375	916	242	0.267	0.283	0.55	0.187	0.218
712-ox1.5	907	235	0.267	0.272	0.539	0.179	0.210
712-ox1.625	906	238	0.265	0.276	0.541	0.182	0.212
712-ox0.83-TPAOH	950	215	0.290	0.323	0.613	0.238	0.266
712-ox1-TPAOH	987	321	0.273	0.468	0.742	0.349	0.392
712-ox1.125-TPAOH	942	400	0.235	0.606	0.842	0.478	0.535
712-ox1.25-TPAOH	985	485	0.227	0.802	1.028	0.666	0.722
712-ox1.375-TPAOH	926	515	0.196	0.993	1.189	0.877	0.927
712-ox1.5-TPAOH	815	593	0.132	1.032	1.165	0.905	0.956
712-ox1.625-TPAOH	814	618	0.125	0.955	1.080	0.791	0.840
712-ox1.125-TBAOH	945	271	0.273	0.400	0.673	0.301	0.340
712-ox1.25-TBAOH	950	330	0.258	0.554	0.812	0.448	0.497
712-ox1.375-TBAOH	932	372	0.240	0.631	0.872	0.524	0.575
712-ox1.5-TBAOH	949	415	0.233	0.785	1.018	0.683	0.728
712-ox1.625-TBAOH	915	396	0.226	0.777	1.003	0.681	0.723

<sup>a</sup> determined from nitrogen physisorption:  $S_{\text{meso}}$  by t-plot method. <sup>b</sup>  $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$

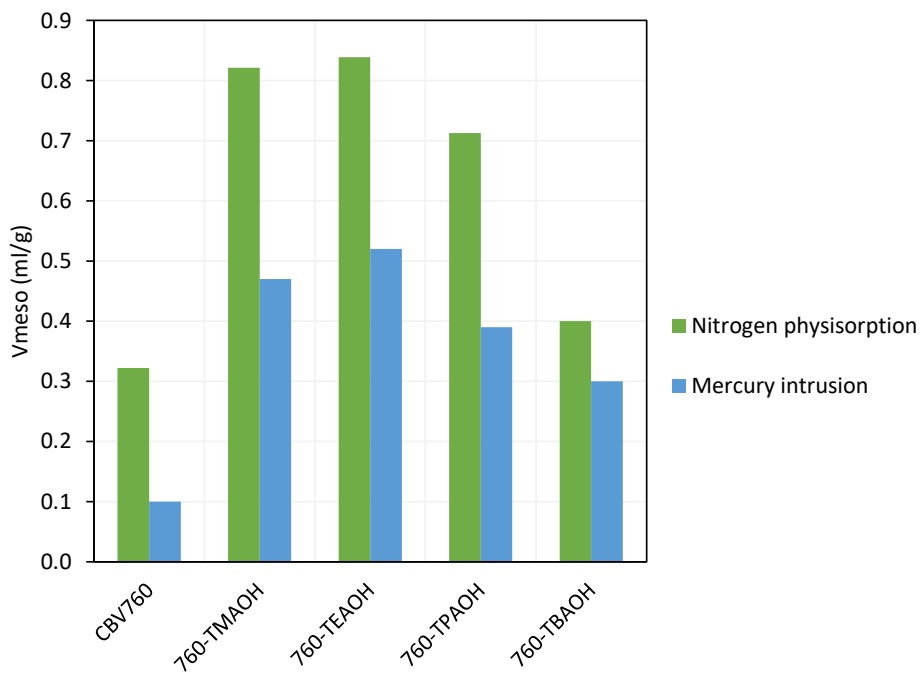


**Figure SI 8.** N<sub>2</sub> physisorption Isotherm curves of (a) 712-ox#, (b) 712-ox#-TPAOH, and (c) 712-ox#-TBAOH samples: the isotherms are offset vertically in steps of 100 ml/g

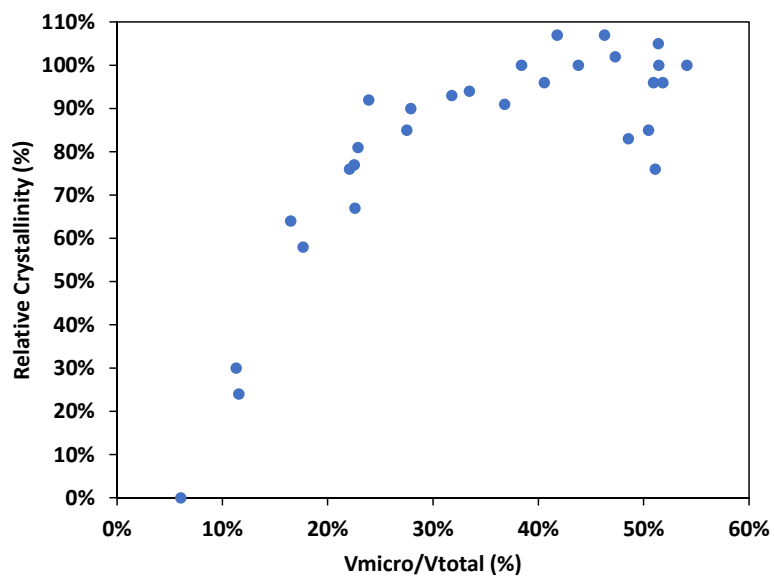




**Figure SI 9.** BJH pore size distribution of (a) 720-TAAOH, (b) 712-ox#-TPAOH and (c) 712-ox#-TBAOH obtained from the desorption curve



**Figure SI 10.** Comparison of measured mesopore volume between nitrogen physisorption and mercury intrusion.



**Figure SI 11.** Relative crystallinity as a function of  $V_{\text{micro}}/V_{\text{total}}$  ( $V_{\text{total}} = V_{\text{micro}} + V_{\text{meso}}$ ).

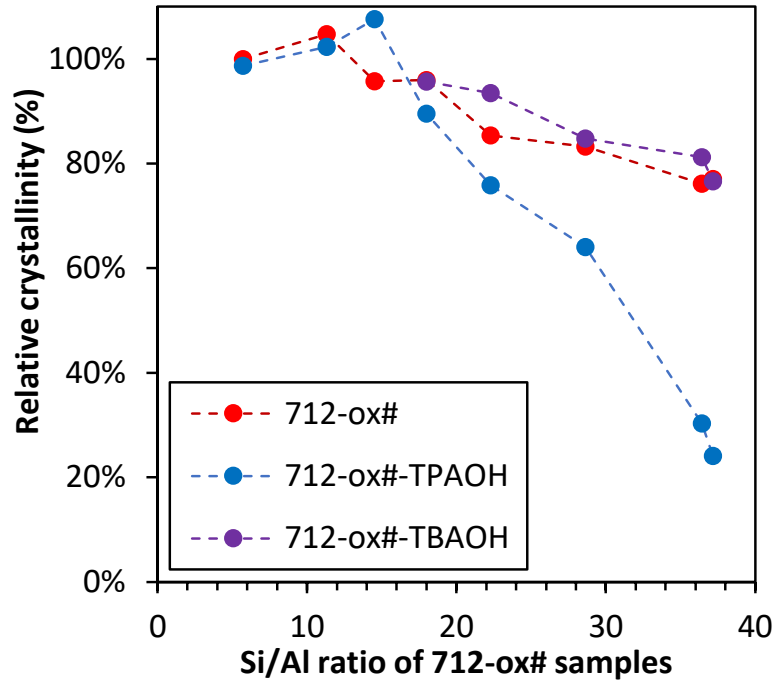
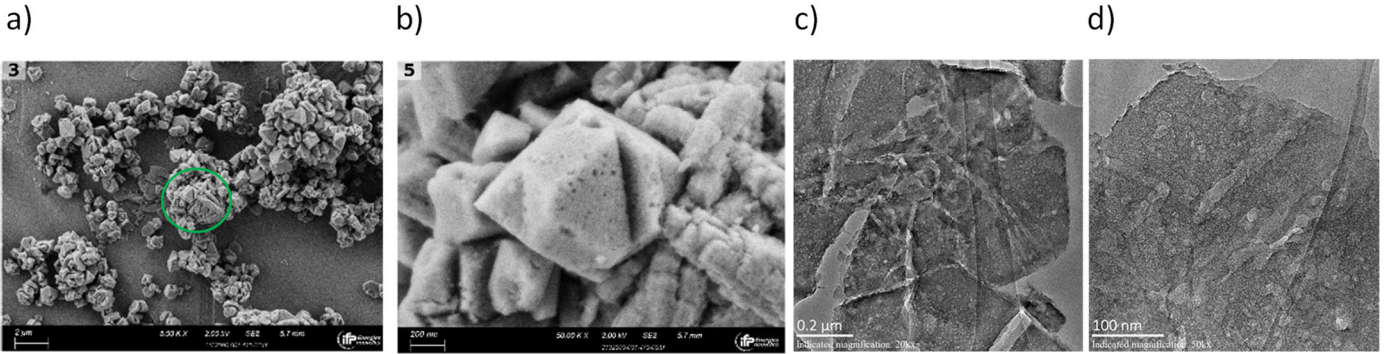


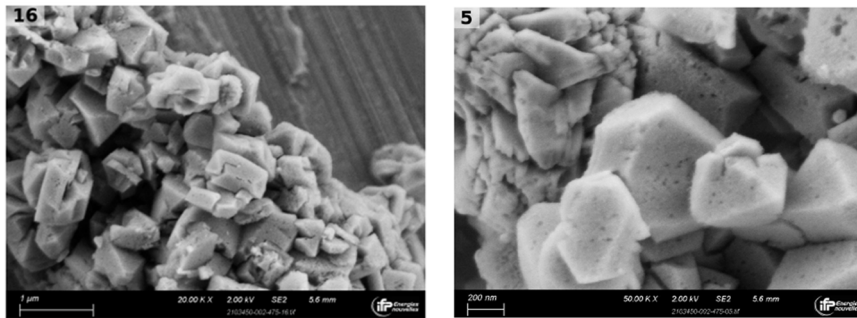
Figure SI 12. Relative crystallinity of modified 712 samples

**Figure SI 13.** SEM and TEM images

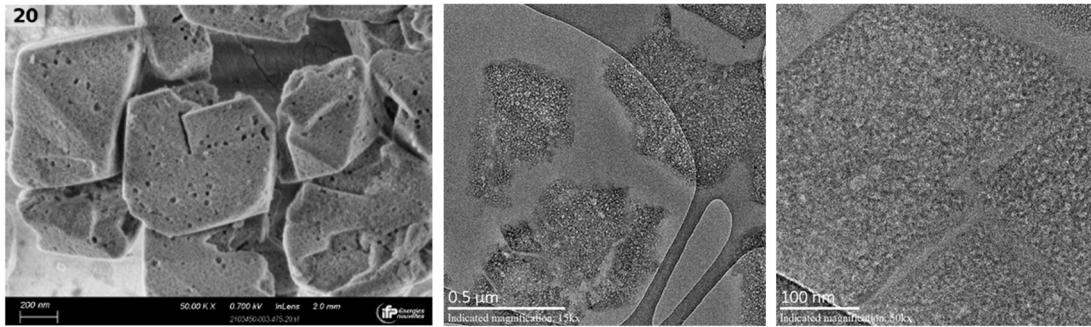
a) CBV760



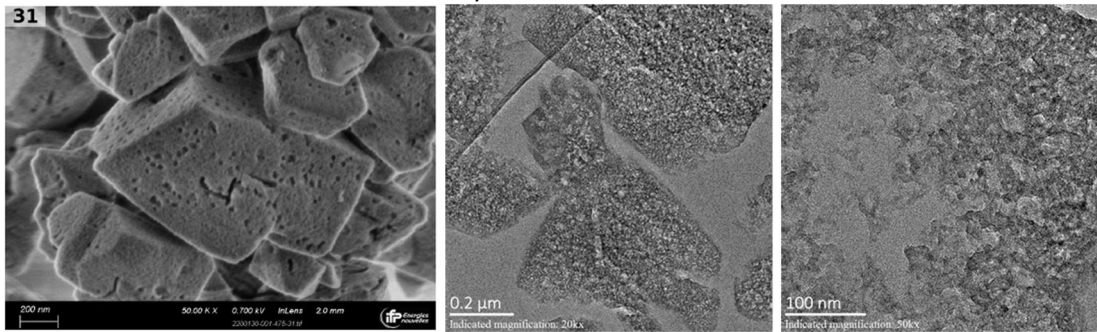
b) 760-TMAOH



c) 760-TEAOH

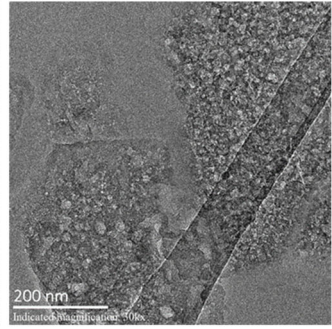
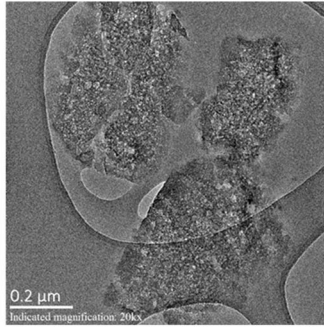
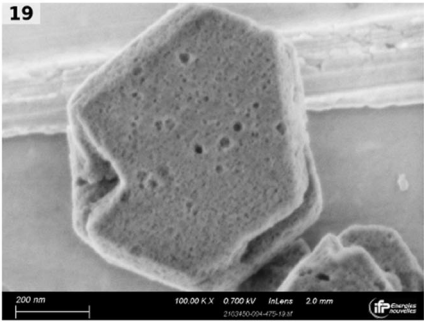


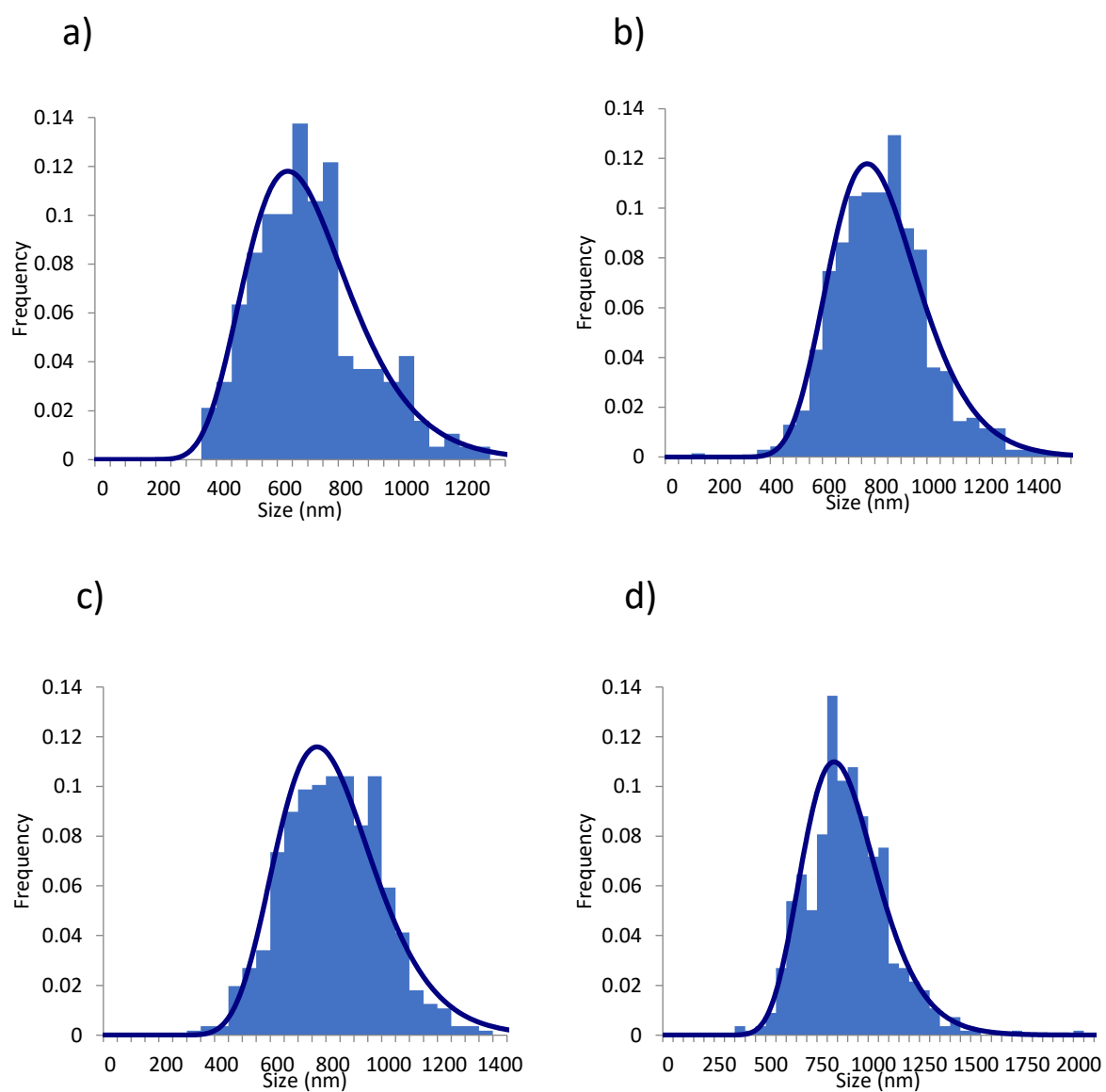
d) 760-TPAOH



e) 760-TBAOH

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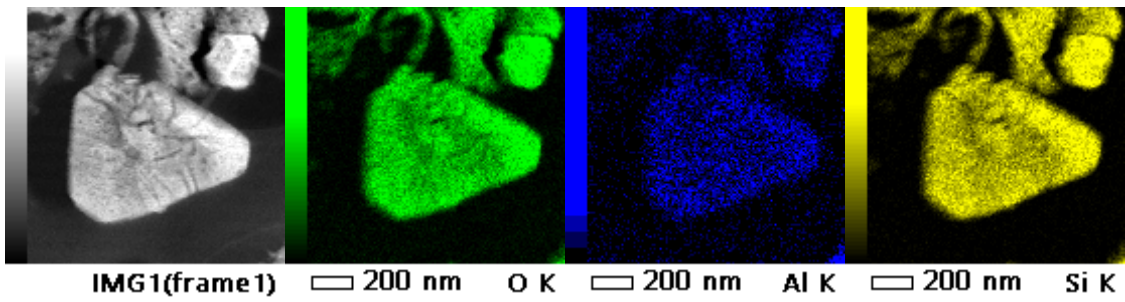




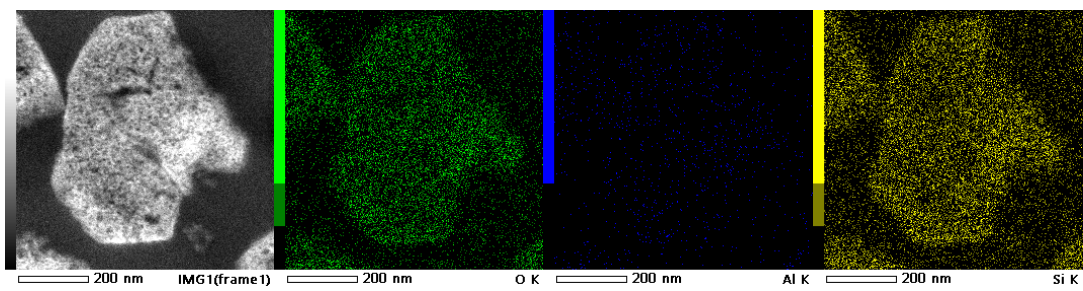
**Figure SI 14.** Distribution of crystal size of (a) CBV760, (b) 760-TEAOH, (c) 760-TPAOH and (d) 760-TBAOH

Figure SI 15. TEM images of a series of 760 samples coupled with EDS

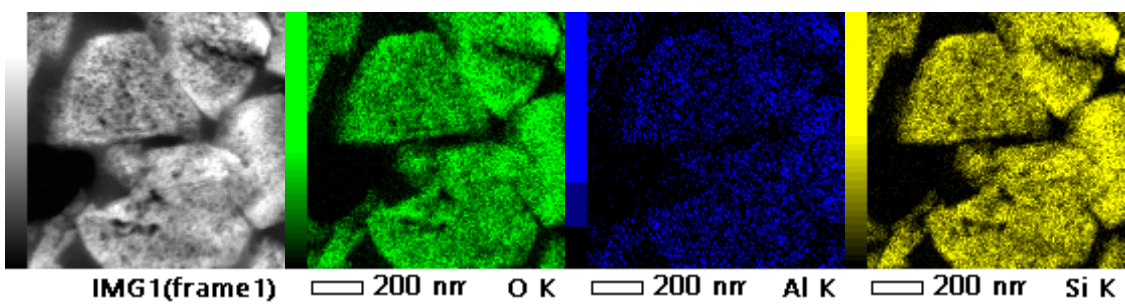
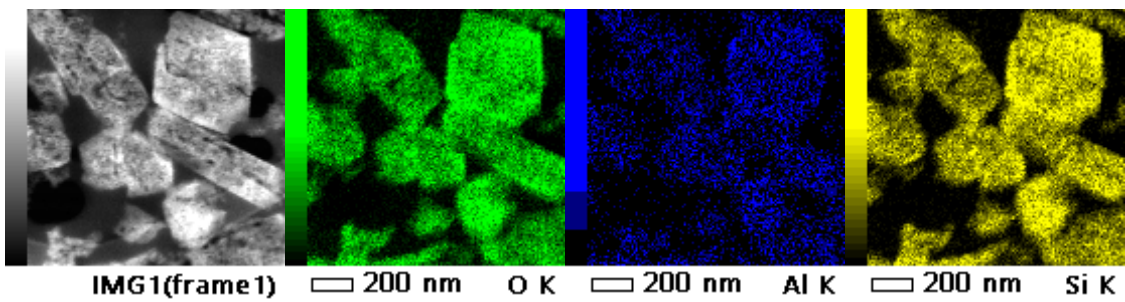
a) CBV760



b) 760-TEAOH



c) 760-TPAOH



d) 760-TBAOH

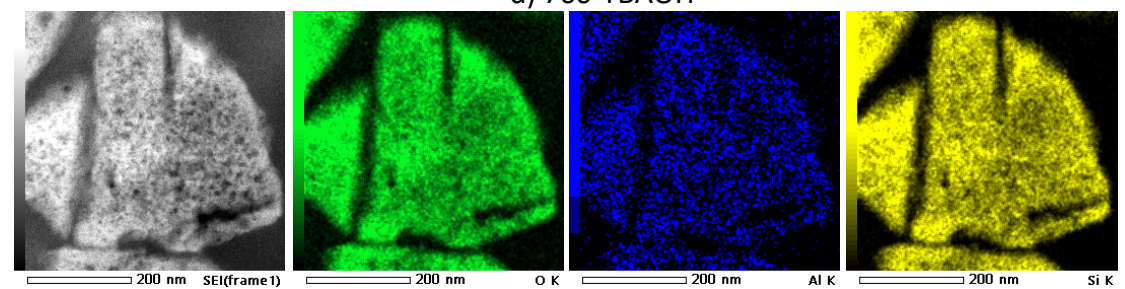
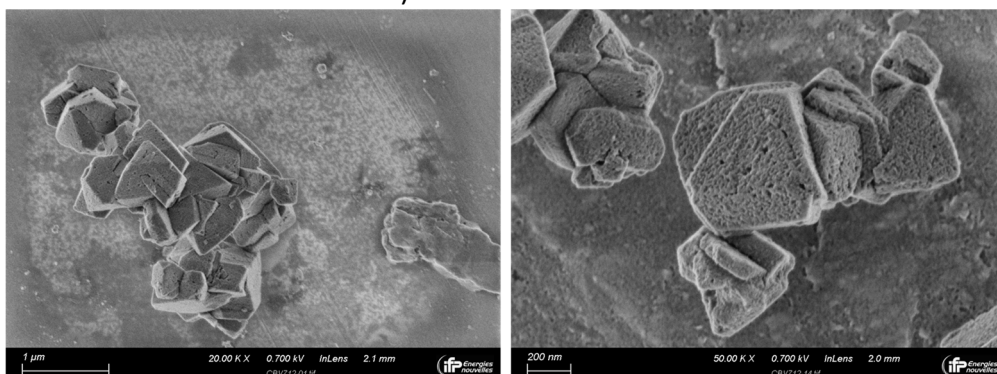
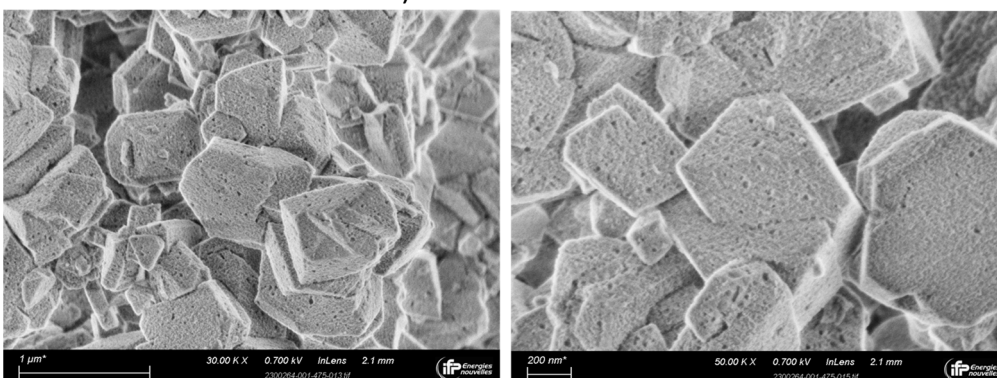


Figure SI 16. SEM images of a series of 712 samples

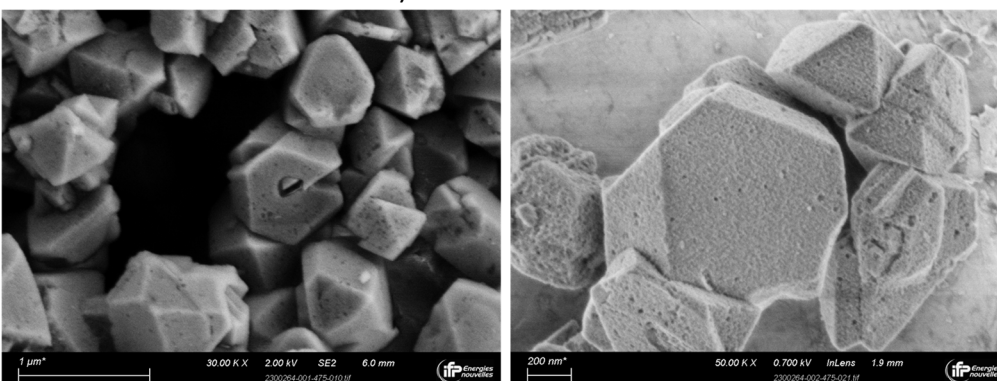
a) CBV712



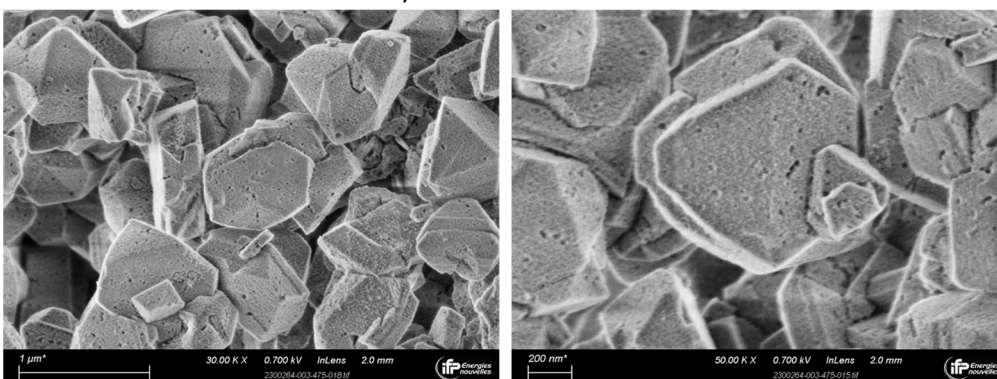
b) 712-ox0.83



c) 712-ox1.25

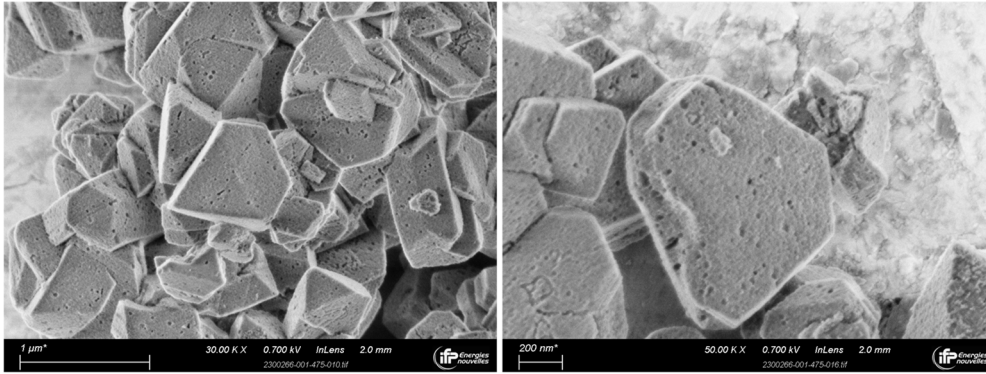


d) 712-ox1.5

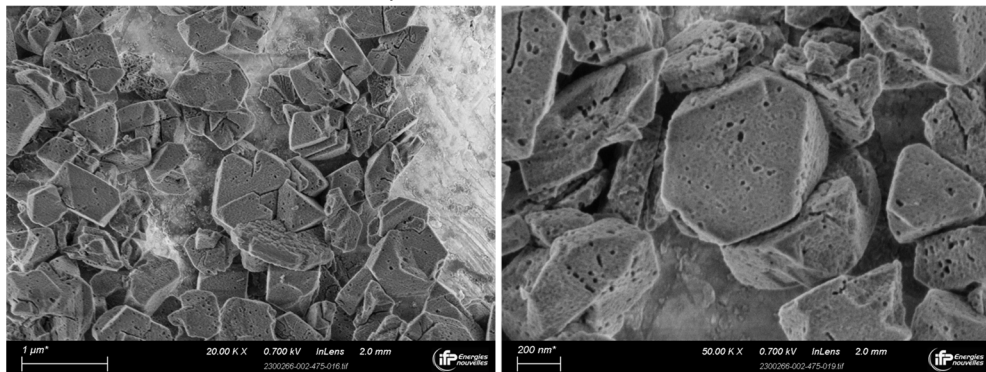




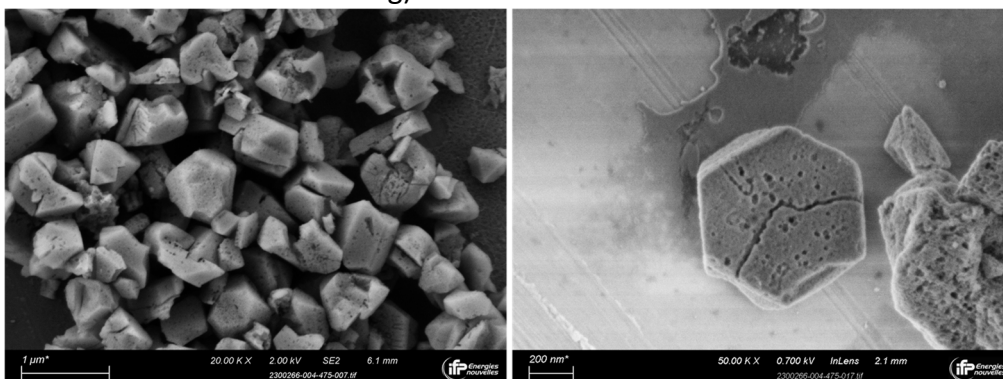
e) 712-TPAOH



f) 712-ox0.83-TPAOH



g) 712-ox1.25-TPAOH



h) 712-1.5-TPAOH

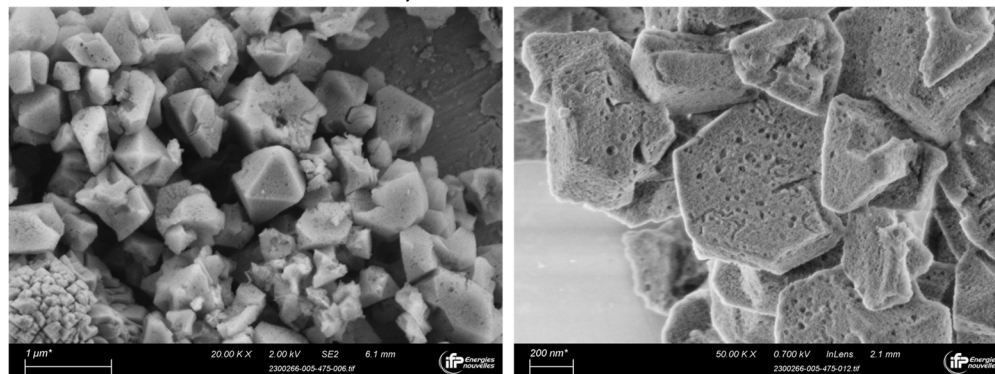
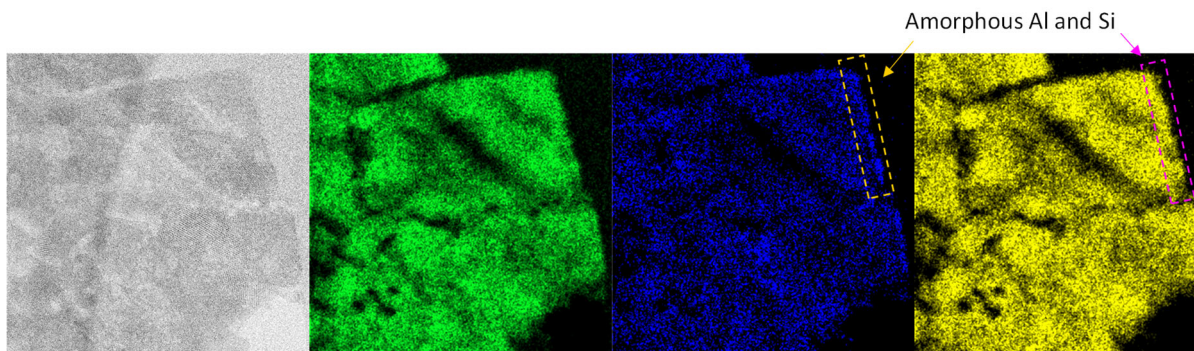
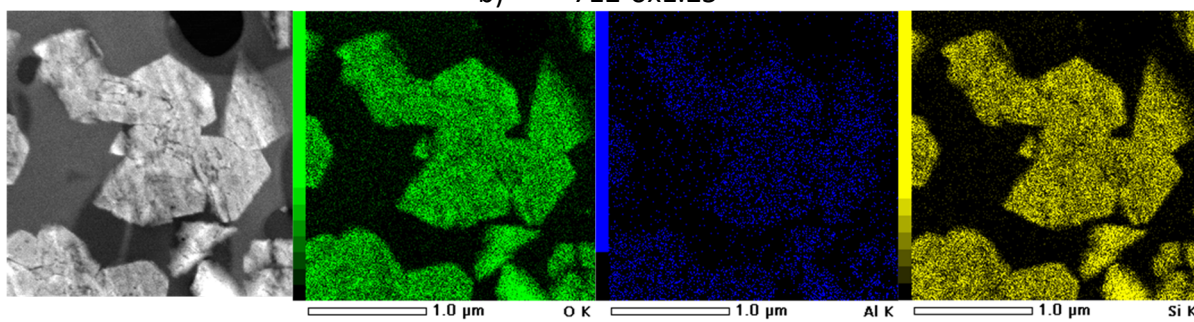


Figure SI 17. TEM images of modified 712 samples coupled with EDS

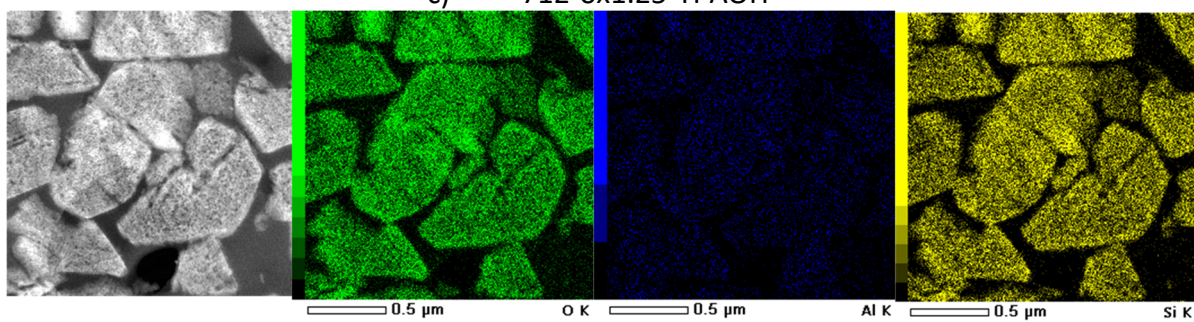
a) CBV712



b) 712-ox1.25



c) 712-ox1.25-TPAOH



**Table SI 18.** The summary of  $^{27}\text{Al}$  MAS NMR analysis

Sample	$\text{Al}_{\text{IV}}$ symmetric	$\text{Al}_{\text{IV}}$ asymmetric	$\text{Al}_{\text{V}}$	$\text{Al}_{\text{VI}}$
CBV760	83%		7%	10%
760-TMAOH	14%	45%	27%	14%
760-TEAOH	48%	29%	10%	13%
760-TPAOH	72%	12%	3%	13%
760-TBAOH	80%	2%	7%	12%
CBV720	53%	24%	3%	20%
720-TMAOH	39%	50%	6%	4%
720-TEAOH	40%	29%	16%	16%
720-TPAOH	51%	21%	10%	18%
720-TBAOH	51%	18%	13%	18%
CBV712	33%	19%	18%	30%
712-ox0.83	54%	27%	10%	10%
712-ox1	58%	19%	11%	12%
712-ox1.125	78%	16%	0%	7%
712-ox1.25	66%	6%	14%	14%
712-ox1.375	84%	0%	9%	7%
712-ox1.5	84%	0%	9%	7%
712-ox0.83-TPAOH	51%	27%	6%	16%
712-ox1-TPAOH	59%	26%	1%	14%
712-ox1.125-TPAOH	61%		12%	28%
712-ox1.25-TPAOH	61%		12%	27%
712-ox1.375-TPAOH	59%		13%	28%
712-ox1.5-TPAOH	50%		16%	34%
712-ox1.625-TPAOH	50%		17%	33%
712-ox1.125-TBAOH	67%		10%	23%
712-ox1.25-TBAOH	66%		10%	24%
712-ox1.375-TBAOH	64%		11%	25%
712-ox1.5-TBAOH	61%		13%	26%
712-ox1.625-TBAOH	64%		12%	24%

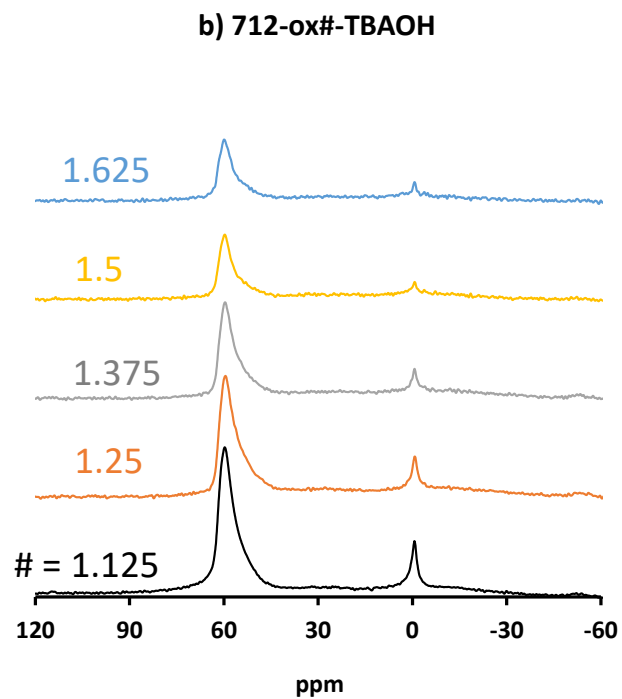
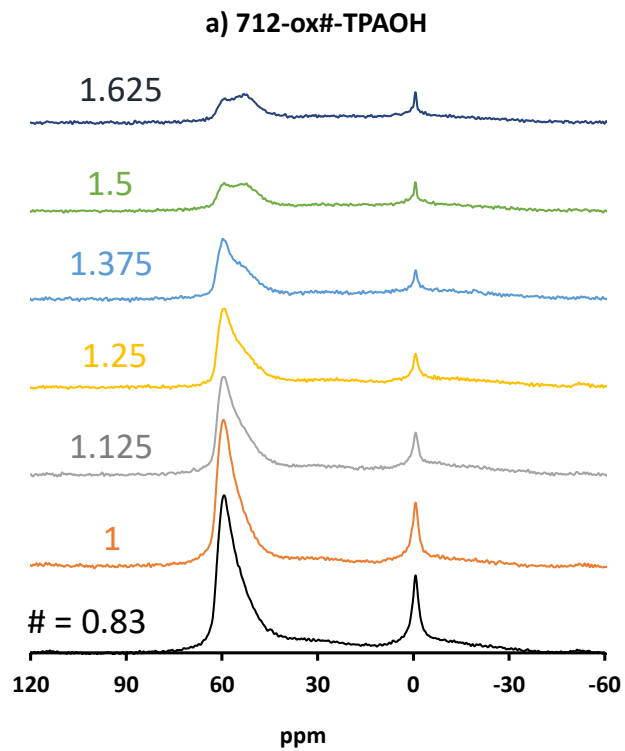
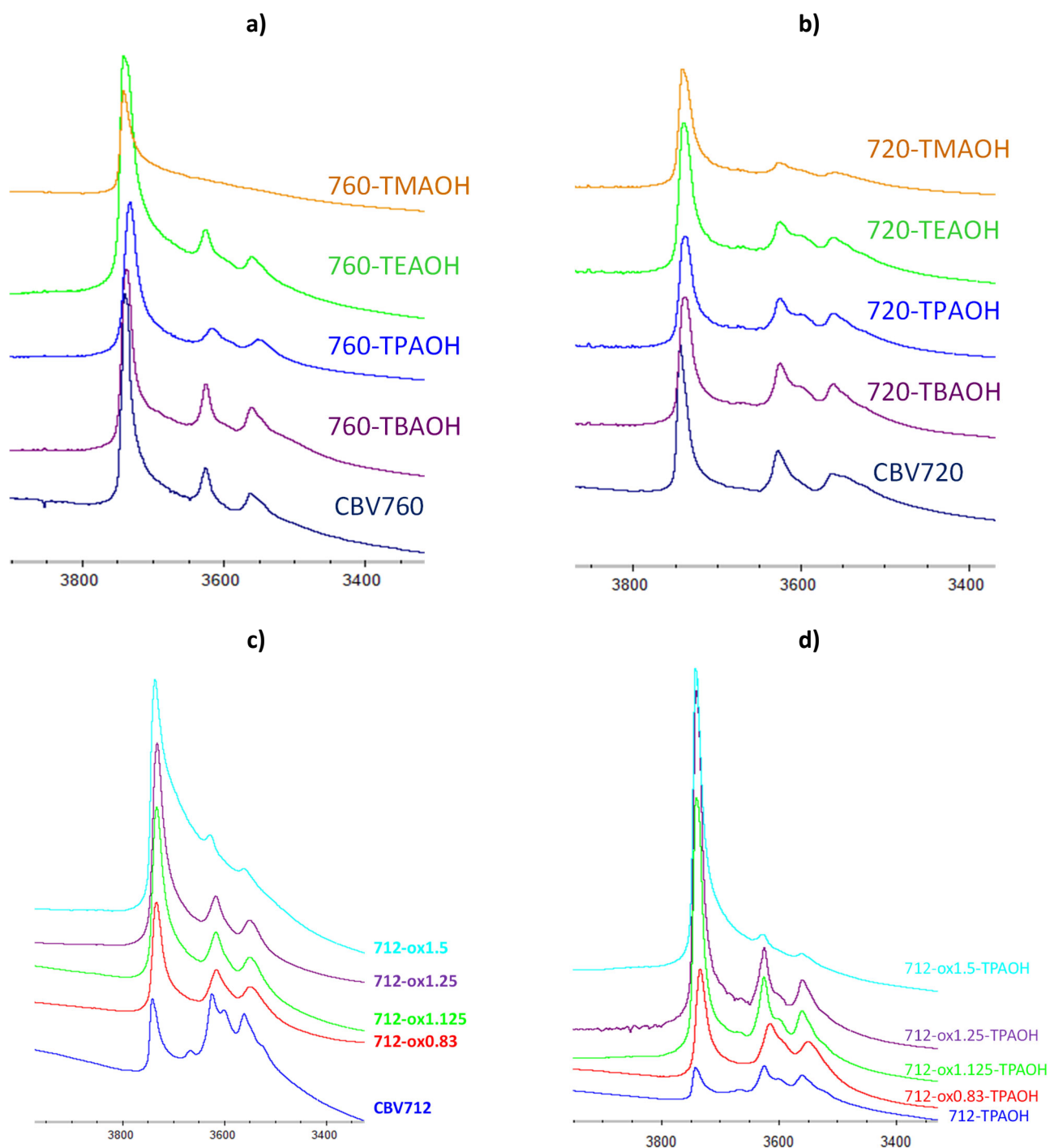


Figure SI 19.  $^{27}\text{Al}$  MAS NMR spectrum of (a) 712-ox#-TPAOH and (b) 712-ox#-TBAOH

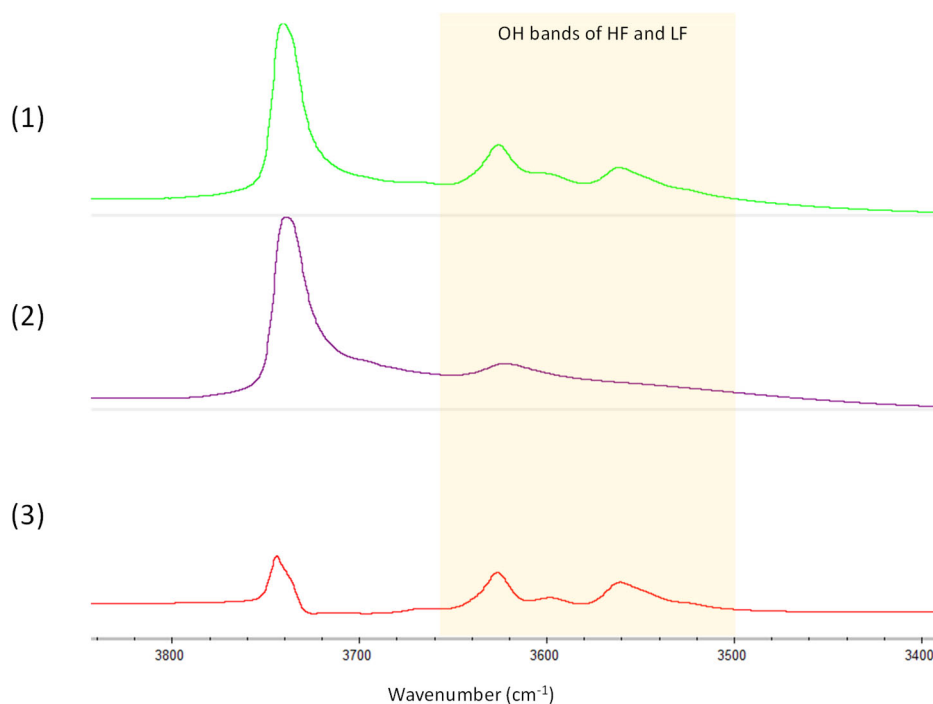


**Figure SI 20.** Altered OH groups of modified a) 760, b) 720, c) 712-ox#, and d) 712-ox#-TPAOH samples. X axis is wavenumber ( $\text{cm}^{-1}$ )

**Table SI 21.** Brønsted- and Lewis acid sites measured by adsorption and desorption of pyridine as a function of temperature. The uncertainty of the value is  $\pm 15\%$ .

sample	Brønsted acid sites ( $[\text{PyH}^+] \mu\text{mol g}^{-1}$ )				Lewis acid sites ( $[\text{PyL}] \mu\text{mol g}^{-1}$ )			
	150 °C	250 °C	350 °C	450 °C	150 °C	250 °C	350 °C	450 °C
CBV760	129	124	90	35	29	25	23	22
760_TMAOH	82	70	43	0	84	71	57	0
760_TEA OH	135	101	64	42	76	61	57	64
760_TPA OH	181	148	88	13	37	30	27	23
760_TBA OH	160	154	133	79	40	32	28	25
CBV720	196	166	96	34	100	71	61	42
720_TMA OH	168	114	52	8	146	104	76	62
720_TEA OH	207	160	101	62	74	56	46	30
720_TPA OH	240	191	123	74	59	45	36	25
720_TBA OH	204	191	116	83	42	39	32	26
CBV712	300	268	191	67	178	109	81	50
712-TMA OH	n.m.							
712-TPA OH	n.m.							
712-ox0.83	220	178	113	31	62	43	30	16
712-ox1	184	136	65	29	61	43	29	12
712-ox1.125	196	168	43	35	25	18	6	4
712-ox1.25	148	130	92	40	16	13	8	6
712-ox1.375	n.m.							
712-ox1.5	89	85	68	36	40	21	18	17
712_ox1.625	n.m.							
712-ox0.83-TPA OH	232	193	123	39	59	37	21	12
712-ox1-TPA OH	199	175	133	73	68	48	38	35
712-ox1.125-TPA OH	247	223	180	92	74	59	51	36
712-ox1.25-TPA OH	223	207	173	88	69	55	47	35
712-ox1.375-TPA OH	n.m.							
712-ox1.5-TPA OH	103	76	41	13	25	23	18	30
712-ox1.625-TPA OH	n.m.							
712-ox1.125-TBA OH	353	315	243	127	136	105	88	82
712-ox1.25-TBA OH	349	311	237	116	146	114	95	86
712-ox1.375-TBA OH	192	180	136	34	48	30	18	9
712-ox1.5-TBA OH	121	113	74	19	23	18	11	8
712-ox1.625-TBA OH	124	110	78	14	31	19	12	6

**Figure SI 22.** Definition and calculation of cBAS



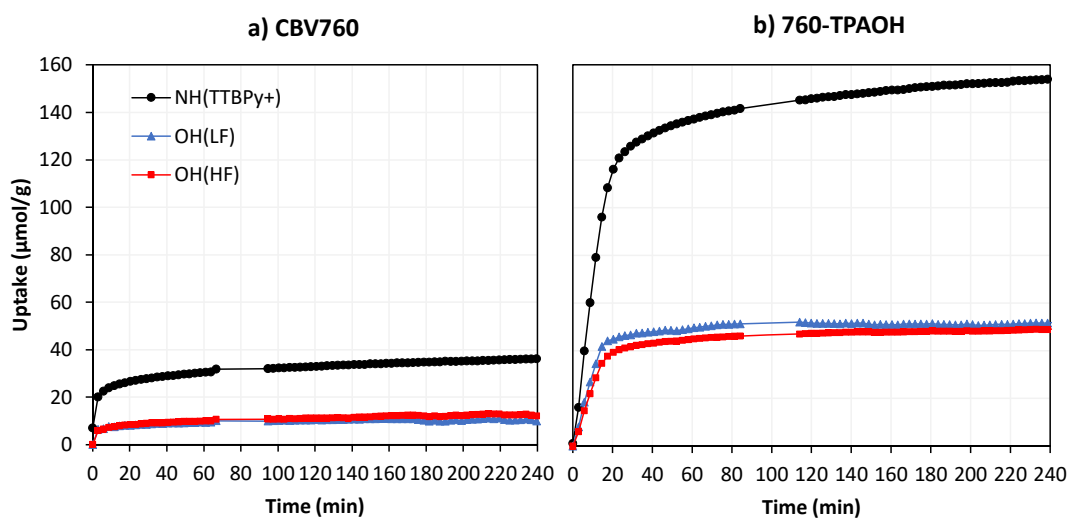
Yellow zone presents OH bands of HF (supercage,  $3625 \text{ cm}^{-1}$  and  $3600 \text{ cm}^{-1}$ ) and LF (sodalite,  $3560 \text{ cm}^{-1}$ )

Spectrum (1) was taken after activation of sample at  $450 \text{ }^\circ\text{C}$ , which shows OH bands after activation  $\rightarrow \text{cBAS}_{\text{int}}$

Spectrum (2) was taken after saturation of probe molecules at  $150 \text{ }^\circ\text{C}$ , which shows OH bands after saturation

Spectrum (3) was obtained by subtraction of (2) from (1), which allows to obtain the concentration of effective Brønsted acid sites  $\rightarrow \text{cBAS}$

**Figure SI 23.** Uptake curve of TTBPY of (a) CBV760 and (b) 760-TPAOH



**Table SI 24.** Hydroxyl groups measured at 450 °C and Brønsted acid sites determined by Pyridine and TTBPY at 150 °C

Samples	Hydroxyl groups (μmol/g)			Measured by Pyridine (μmol/g)			Measured by TTBPY (μmol/g)			
	OH <sub>HF</sub>	OH <sub>LF</sub>	cBAS <sub>int</sub> (=OH <sub>HF</sub> +OH <sub>LF</sub> )	BAS total [PyH <sup>+</sup> ]	cBAS <sub>Py</sub>	pBAS <sub>Py</sub>	BAS <sub>acc</sub> [TTBPYH <sup>+</sup> ]	cBAS <sub>acc</sub>	pBAS <sub>acc</sub>	Accessibility TTBPY (ACI <sub>TTBPY</sub> ) (%)
CBV760	48	69	117	164	109	55	36	30	5	26%
760-TMAOH	0	0	0	82	0	82	86	0	86	0%
760-TEAOH	32	34	65	135	63	72	146	47	99	72%
760-TPAOH	66	87	153	182	122	60	154	100	54	65%
760-TBAOH	51	100	151	160	160	0	125	58	66	39%
CBV720	92	186	278	197	236	-39	43	53	-10	19%
720-TMAOH	31	38	69	168	81	87	149	54	95	79%
720-TEAOH	66	90	156	207	160	47	143	88	55	56%
720-TPAOH	83	112	195	241	207	34	78	65	14	33%
720-TBAOH	104	140	243	205	197	8	57	49	8	20%
CBV712	182	331	513	301	262	39	30	0	30	0%
712-ox0.83	109	130	238	220	81	139	41	28	13	12%
712-ox1	120	168	289	184	165	19	78	81	-4	28%
712-ox1.25	67	61	129	148	79	69	114	59	54	46%
712-ox1.5	30	34	64	89	21	68	59	37	22	58%
712-TPAOH	156	236	393	231	127	104	29	26	3	7%
712-ox0.83-TPAOH	136	155	291	279	154	126	82	61	21	21%
712-ox1-TPAOH	141	164	305	200	129	71	200	154	46	50%
712ox1.25-TPAOH	98	102	200	224	141	83	222	153	69	77%
712ox1.5-TPAOH	24	26	50	100	20	80	120	45	76	90%
712ox1.25-TBAOH	122	159	281	350	286	65	179	160	19	57%
712ox1.5-TBAOH	66	113	179	122	98	23	120	105	15	59%



**Figure SI 25.** [cBAS] and [pBAS] measured with Py and TTBPY for a series of (a) 760, (b) 720, (c) 712-ox#, and (d) 712-ox#-TPAOH samples.

