Supplementary Information

Aqueous HF-$HBrO_4$ Solutions for Wet-Chemical Etching of (100) Silicon Wafer Surfaces

Nils Schubert[a,c], Niklas Zomack[a,c], André Stapf[a,c], Patrick Fuzon[b], Ann-Lucia Neumann[a,c], Dominic Walter[d], Andreas Lißner[d], Florian Kraus[b], Edwin Kroke[a,c,]*

a) Institute of Inorganic Chemistry, Technische Universität Bergakademie Freiberg, Leipziger Str. 29, D-09599 Freiberg, Germany

b) Research Group for Inorganic Chemistry, Philipps-University of Marburg, Hans-Meerwein-Strasse 4, D-35043 Marburg, Germany

c) Centre for Efficient High-Temperature Material Conversion, Technische Universität Bergakademie Freiberg, Winklerstr. 5, D-09599 Freiberg, Germany

d) Institute of Physical Chemistry, Technische Universität Bergakademie Freiberg, Leipziger Str. 29, D-09599 Freiberg, Germany

*Corresponding author: Prof. Dr. Edwin Kroke, edwin.kroke@chemie.tu-freiberg.de

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1 Data of the Prepared $HBrO_4$

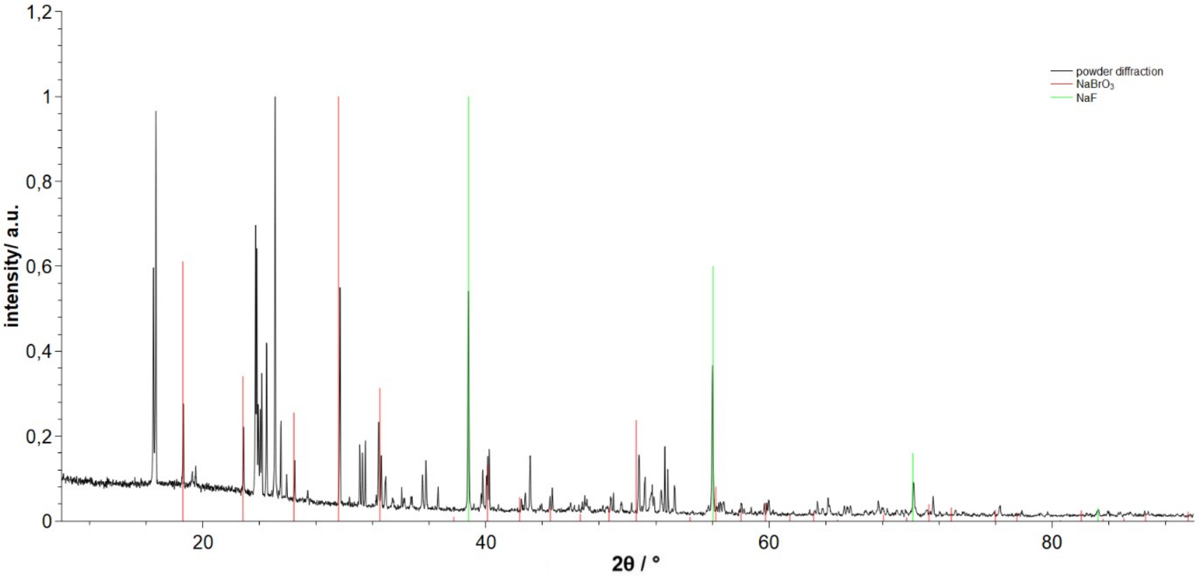

Figure S1. Powder diffractogram of the crude product after passing F_2 into the solution, the reflexes of the starting material $NaBrO_3$ (red) and the side product NaF (green) are clearly visible.

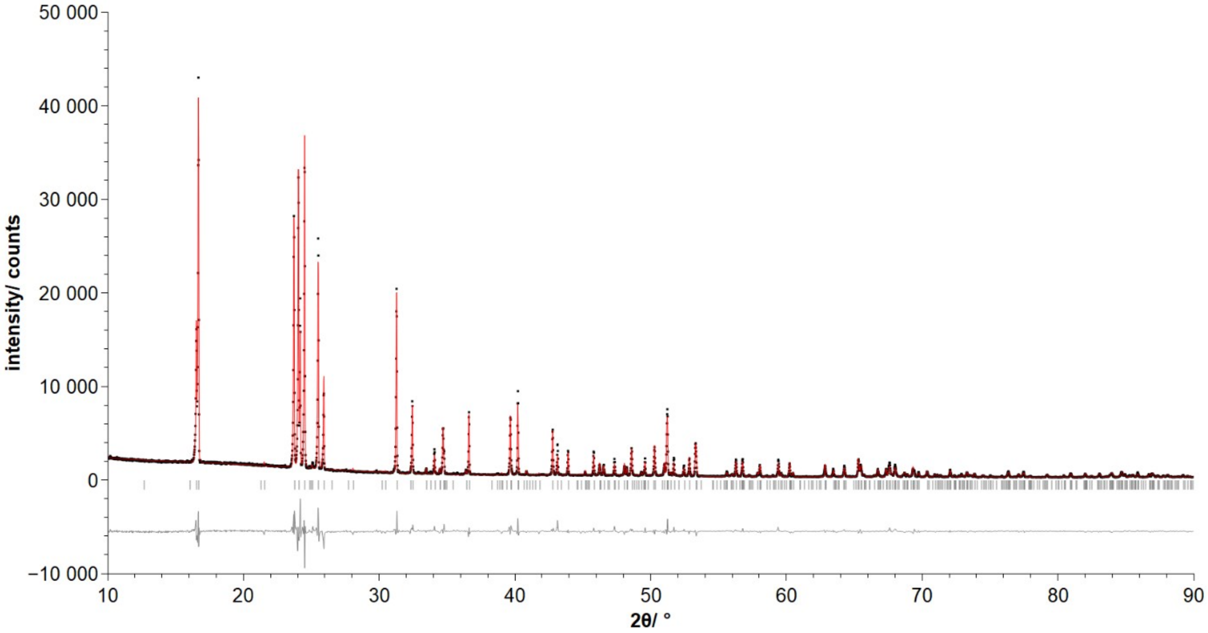

Figure S2. Powder diffractogram of the purified $NaBrO_4 \cdot H_2O$ with Rietveld refinement.

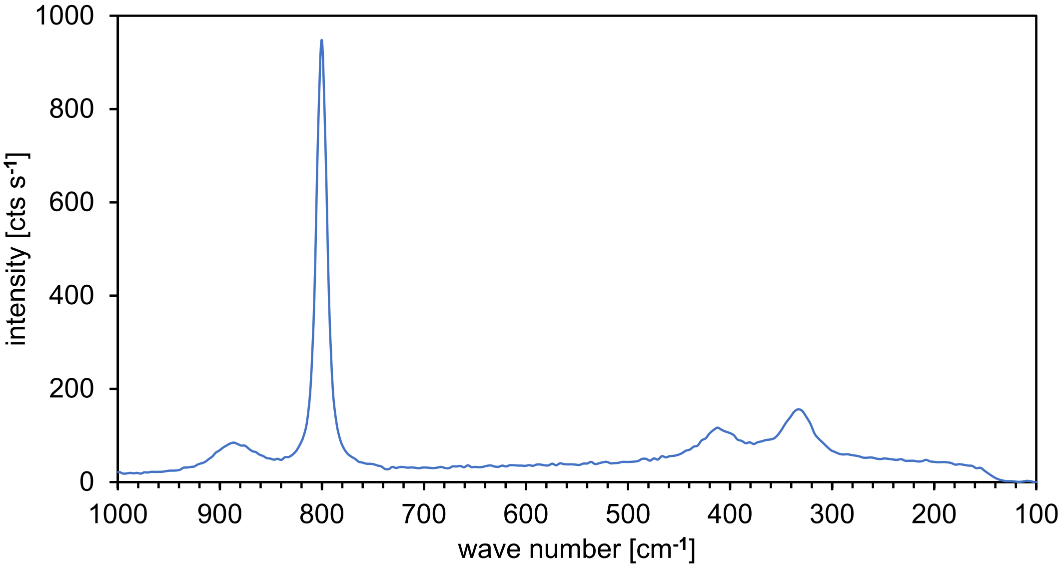

Figure S3. Raman spectrum of a 1 M $NaBrO_4$ solution, showing the characteristic valence vibrations of the perbromate anions at 331, 410, 798 & 883 cm^{-1}.[64] A minor Br_2 content could be derived from the shoulder at 315 cm^{-1}.[45]

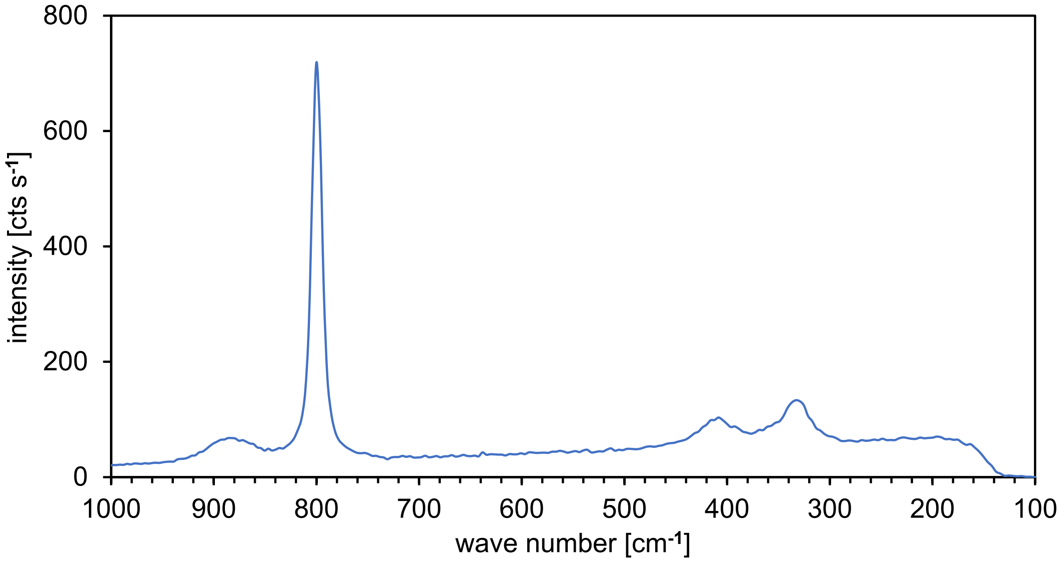

Figure S4. Raman spectrum of the crude $HBrO_4$ solution after ion exchange.

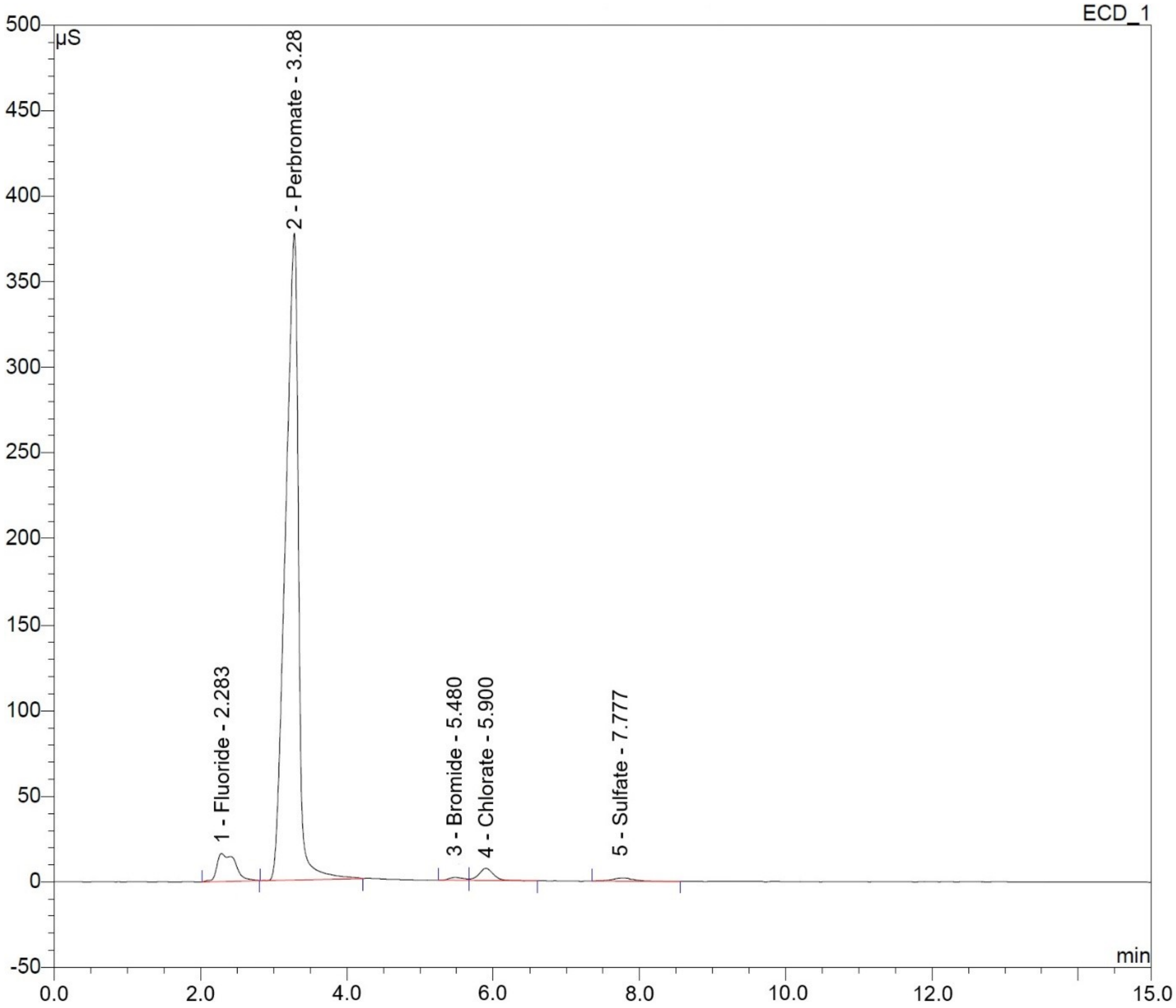

Figure S5. Ion chromatogram of the $HBrO_4$ used for the experiments.

2 Additional SEM Pictures

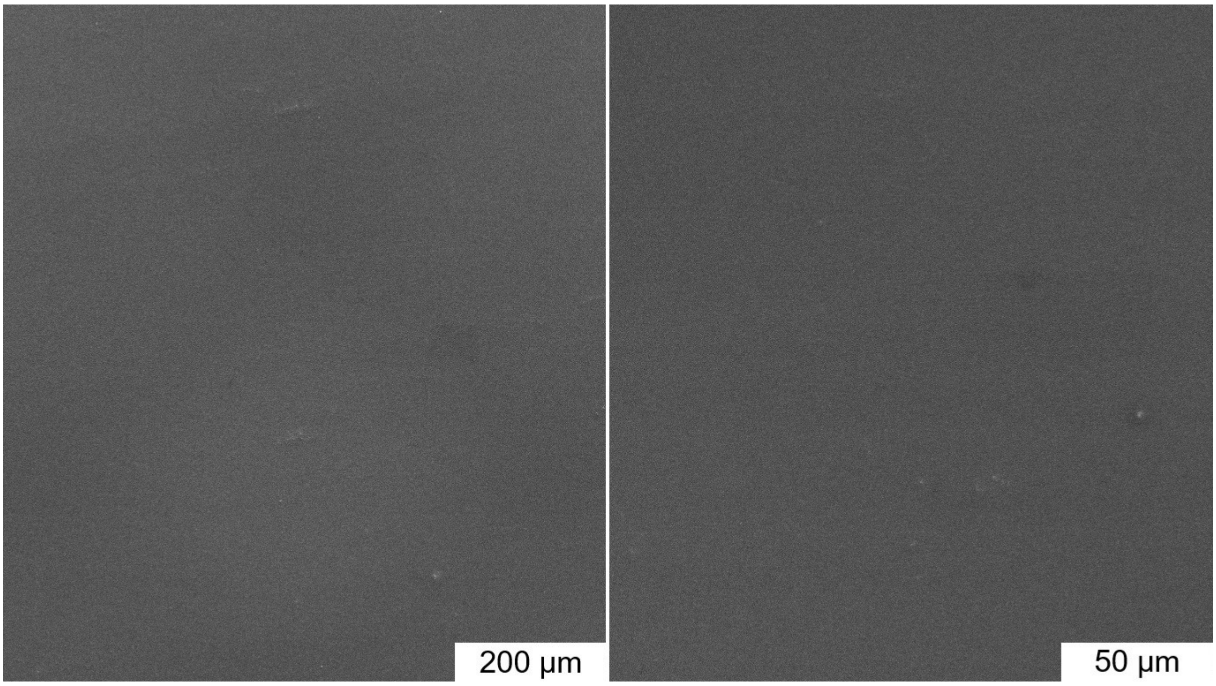

Figure S6. SEM images of a silicon (100) surface, etched in a mixture containing c(HF) = 14.6 mol L^{-1}, c($HBrO_4$) = 0.5 mol L^{-1} at 100 °C without N_2 introduction, with 300 rpm of stirring for 5 min, Δd = 23.2 µm.

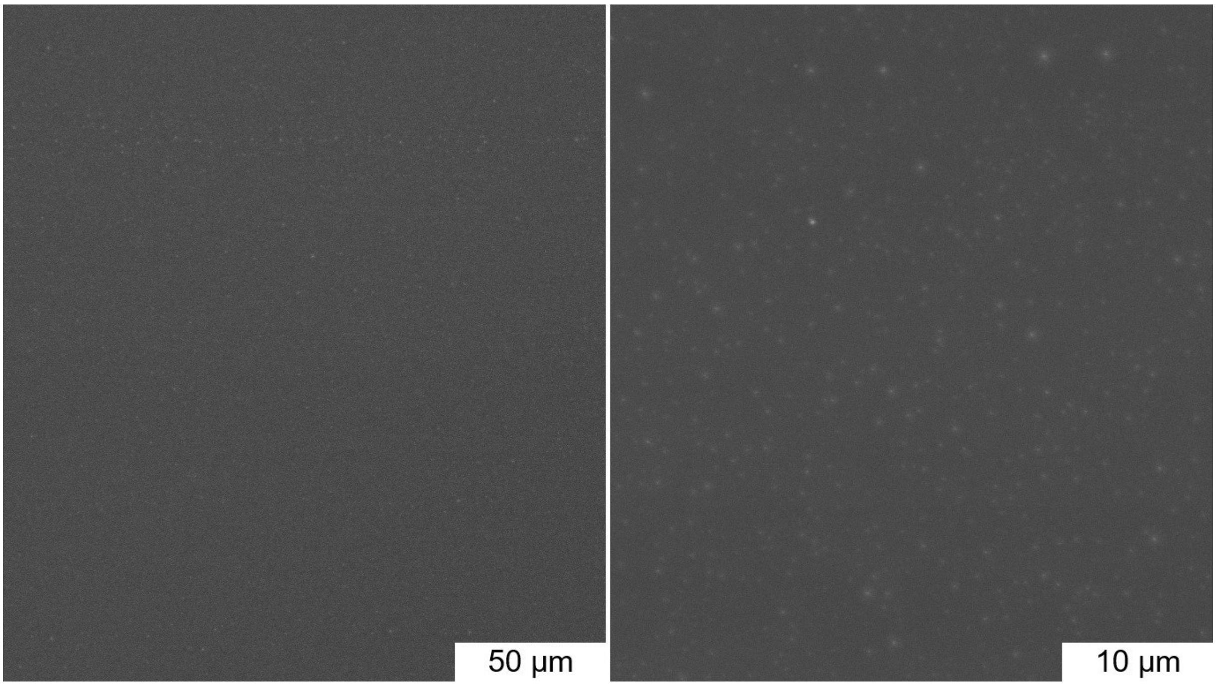

Figure S7. SEM images of a silicon (100) surface, etched in a mixture containing c(HF) = 14.6 mol L^{-1}, c($HBrO_4$) = 0.5 mol L^{-1} at 60 °C with N_2 introduction & 300 rpm of stirring for 10 min, Δd = 43.6 µm.

3 Data of the Etching Experiments in Aqueous HF-HBrO$_4$ Solutions

Table S1. Experimental data of the HF-HBrO$_4$ etching experiments.

VP	RUN	HF [50%]	HF [50%]	HF	HBrO$_4$ [1M]	HBrO$_4$ [1M]	HBrO$_4$	V(total)	T	t_{etch}	m_0	m_1	dm	dd per side	r per side	A	$\bar{r}$ per side	A(wafer)	m(wafer)	N$_2$ introduction
		mL	Vol-%	mol/L	mL	Vol-%	mol/L	mL	°C	min	g	g	g	µm	µm/min	cm²	µm/min	cm²	g	
I	1	30	75	21.91	10	25	0.25	40	20	10	0.0704	0.0602	0.0102	12.60	1.26	1.73	0.61	242.14	9.8364	no N$_2$ introduction
	2									20	0.0708	0.0548	0.0160	19.65	0.98	1.74				
	3									20	0.0600	0.0575	0.0025	3.62	0.18	1.48				
	4									120	0.0504	0.0481	0.0023	3.97	0.03	1.24				
II	1	30	75	21.91	10	25	0.25	40	20	20	0.0582	0.0582	0.0000	0.00	0.00	1.43	0.01			no N$_2$ introduction
	2									180	0.0617	0.0597	0.0020	2.82	0.02	1.52				
	3									1080	0.0466	0.0356	0.0110	20.52	0.02	1.15				
III	1	30	75	21.91	10	25	0.25	40	80	10	0.0402	0.0380	0.0022	4.76	0.48	0.99	0.48			no N$_2$ introduction
IV	1	30	50	14.61	30	50	0.5	60	100	45	0.0645	0.0000	0.0645	86.95	1.93	1.59	3.31			with N$_2$ introduction
	2									10	0.0657	0.0261	0.0396	52.41	5.24	1.62				
	3									5	0.0893	0.0656	0.0237	23.08	4.62	2.20				
	4									2	0.0749	0.0680	0.0069	8.01	4.01	1.84				
	5									2	0.0852	0.0779	0.0073	7.45	3.72	2.10				
	6									3	0.0937	0.0827	0.0110	10.21	3.40	2.31				
	7									4	0.1076	0.0941	0.0135	10.91	2.73	2.65				
	8									5	0.1108	0.0960	0.0148	11.61	2.32	2.73				
	9									10	0.1254	0.0997	0.0257	17.82	1.78	3.09				
V	1	30	50	14.61	30	50	0.5	60	100	10	0.0995	0.0105	0.0890	77.77	7.78	2.45	3.14			no N$_2$ introduction
	2									5	0.0756	0.0554	0.0202	23.23	4.65	1.86				
	3									7.5	0.0714	0.0572	0.0142	17.29	2.31	1.76				
	4									5	0.0617	0.0554	0.0063	8.88	1.78	1.52				
	5									10	0.0448	0.0376	0.0072	13.97	1.40	1.10				
	6									20	0.0664	0.0521	0.0143	18.73	0.94	1.63				
VI	1	30	50	14.61	30	50	0.5	60	60	10	0.0425	0.0212	0.0213	43.58	4.36	1.05	2.46			with N$_2$ introduction
	2									10	0.0534	0.0255	0.0279	45.43	4.54	1.31				
	3									10	0.0599	0.0337	0.0262	38.03	3.80	1.47				
	4									10	0.0699	0.0445	0.0254	31.60	3.16	1.72				
	5									15	0.0475	0.0273	0.0202	36.98	2.47	1.17				
	6									20	0.0696	0.0319	0.0377	47.10	2.35	1.71				
	7									20	0.0582	0.0394	0.0188	28.09	1.40	1.43				
	8									20	0.0504	0.0373	0.0131	22.60	1.13	1.24				
	9									30	0.0789	0.0557	0.0232	25.57	0.85	1.94				
	10									10	0.0798	0.0746	0.0052	5.67	0.57	1.96				

Continuation of Table S1. Experimental data of the HF-$HBrO_4$ etching experiments.

VP	RUN	HF [50%]	HF [50%]	HF	$HBrO_4$ [1M]	$HBrO_4$ [1M]	$HBrO_4$	V(total)	T	t_{etch}	m_0	m_1	dm	dd per side	r per side	A	$\overline{r}$ per side	A(wafer)	m(wafer)	N_2 introduction
		mL	Vol-%	mol/L	mL	Vol-%	mol/L	mL	°C	min	g	g	g	µm	µm/min	cm²	µm/min	cm²	g	
VII	1	30	50	14.61	30	50	0.5	60	20	10	0.0684	0.0544	0.0140	17.80	1.78	1.68	0.95	242.14	9.8364	with N_2 introduction
	2									20	0.0675	0.0458	0.0217	27.95	1.40	1.66				
	3									30	0.0648	0.0389	0.0259	34.75	1.16	1.60				
	4									30	0.0659	0.0489	0.0170	22.43	0.75	1.62				
	5									20	0.0620	0.0578	0.0042	5.89	0.29	1.53				
	6									10	0.0601	0.0580	0.0021	3.04	0.30	1.48				
VIII	1	30	50	14.61	30	50	0.5	60	40	10	0.0593	0.0381	0.0212	31.08	3.11	1.46	2.16			with N_2 introduction
	2									10	0.0716	0.0490	0.0226	27.44	2.74	1.76				
	3									15	0.0680	0.0417	0.0263	33.63	2.24	1.67				
	4									15	0.0526	0.0345	0.0181	29.92	1.99	1.29				
	5									20	0.0554	0.0349	0.0205	32.17	1.61	1.36				
	6									30	0.0622	0.0354	0.0268	37.46	1.25	1.53				
IX	1	30	50	14.61	30	50	0.5	60	80	10	0.0538	0.0129	0.0409	65.84	6.58	1.33	3.85	242.14	9.798	with N_2 introduction
	2									10	0.0621	0.0241	0.0380	53.00	5.30	1.53				
	3									10	0.0651	0.0296	0.0355	47.23	4.72	1.61				
	4									10	0.0671	0.0387	0.0284	36.66	3.67	1.66				
	5									10	0.0808	0.0545	0.0263	28.19	2.82	2.00				
	6									15	0.0743	0.0456	0.0287	33.46	2.23	1.84				
	7									20	0.0554	0.0349	0.0205	32.05	1.60	1.37				

4 Additional Information Regarding DRIFTS Measurements

Table S2. IR vibrational bands of selected compounds.

Compound	Group	Wave number [cm^{-1}]	Assignment	Literature
H_2O	OH_2	3734	B_2	45
		3638	A_1	
		1589	A_1 (δ)	
CO_2	O_2C	2349	Σ_u	45
		1343	Σ_g	
		667	Π_u (δ)	
HCOOH	HC	2943	A'	45
OHC-CHO	HC	2843	A_g	45
		2835	B_u	
$H_2C{=}O$	H_2C	2843	B_1	45
		2782	A_1	
H_3C-OH	H_3C	2973	A''	45
		2845	A'	
Me_3SiH	HSi	2118	A_1	45
Me_2SiH_2	H_2Si	2145	B_1	45
		2142	A_1	
$MeSiH_3$	H_3Si	2169	A_1	45
		2166	E	
$HSi(O)_2$-O-$Si(O)_2H$	HSi(O)	2249	A_1	41
		2252	A_2	
		868	A_1 (δ)	
Me_3SiOH	OSi	1254	A_1	65
SiO_2	O_2Si	1416	Σ_u	45
$HSi(OMe)_3$	O_3Si	790	E	45
		700	A_1	
$Si(OMe)_4$	O_4Si	843	F_2	45
		642	A_1	
F_3Si-O-SiF_3	OSi_2	1206	B_1	45
		598	A_1	
$(Me_2SiO)_3$	OSi_2	1034	E'	45
		609	E'	
		585	A_1'	
$FSiH_3$	FSi	892	A_1	45
F_2SiH_2	F_2Si	981	B_2	45
		897	A_1	
F_3SiH	F_3Si	999	E	45
		859	A_1	
F_3Si-SiF_3	F_3Si	985	E_u	45
		971	E_g	
		910	A_{1g}	
		819	A_{2u}	
F_3Si-O-SiF_3	F_3Si	993	A_2	45
		989	B_1	
		949	A_1	
		634	A_1	
SiF_4	F_4Si	1030	F_2	45
		801	A_1	
		389	F_2 (δ)	
		264	E (δ)	