Supplementary Information

Strategies to Passivate Brønsted Acidity in Nb-TUD-1 Enhance Hydrogen Peroxide Utilization and Reduce Metal Leaching during Ethylene Epoxidation

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Table S1: ^{29}Si MAS NMR analysis of parent Nb-TUD-1 and capped catalysts

Entry	Catalyst	Q2	Q3	Q4	(Q2+Q3)/Q4
1	Nb (200)	46.0	183.7	45.6	5.04
2	Nb (40)	28.4	321.0	73.5	4.75
3	NR_4-Nb (200)	21.6	286	180.2	1.7
4	NHR_3-Nb (200)	43.8	262	133.3	2.29
5	Bn-Nb (40) (B-1)	60.9	441	133.1	3.77
6	Me-Nb (200)	10.5	204.8	43.1	4.99
7	TMS-Nb (40)	32.6	269	104	2.9
8	t-Bu-Nb (40)	24	395	250	4.02

Table S2: Thermal gravimetric analysis results (exotherms) of capped and parent Nb-TUD-1 catalysts (T ramped from 22-800 °C)

Samples	Exothermic peaks								Total mass loss (%)
	T °C	Mass Loss (%)	T °C	Mass Loss (%)	T °C	Mass Loss (%)	T °C	Mass Loss (%)	
Bn-Nb(40)	100	7	408	5.8	494	0.9	678	0.8	16
Me-Nb(40)	70	2.2	400	1.6	510	5.3	n		10
Me-Nb(200)	66	1.6	341	1.8	540	3.2	n		7.8
Nb(200)	69	1.5	299	0.3	n		n		2.6
Nb(40)	71	3.2	286	0.5	n		n		5.3
R_3NH-Nb(200)	67	2.6	335	1.4	578	1.8	n		7.7
R_4N-Nb(200)	72	1.5	208	9.5	520	1.2	n		15.7
t-Bu-Nb(40)	69	3.1	166	0.6	397	4.6	530	2.4	12.6
TMS-Nb(40)	72	1.9	287	1.7	478	2.1	n		7

“n” stands for no peak observed

Table S3. Extent of H_2O_2 decomposition on silica support, parent catalyst and capped catalysts (Conditions: 2 g of 50 % aq. H_2O_2, material amount = 0.1 g, 48-50 h, no stirring)

Entry	Catalysts	Initial [H_2O_2] (%)	Final [H_2O_2] (%)	H_2O_2 decomposition[a] (%) (±3 %)
1	Si-TUD-1	49.7	49.9	NIL
2	Nb(200)	49.5	11.2	77.3
3	Nb(40)	49.7	1.0	98.0
4	NHR_3-Nb(200)	49.5	41.4	16.5
5	NR_4-Nb(200)	49.5	47.7	3.7
6	Me-Nb(200)	49.7	45.4	8.5
7	Bn-Nb(40)	49.7	48.6	2.2
8	TMS-Nb(40)	49.7	6.8	86.
9	t-Bu-Nb(40)	49.7	1.2	97.7
10	Nb(200)[b]	14.3	13.7	3.7
11	NHR_3-Nb(200)[b]	49.7	49.9	NIL

[a]H_2O_2 decomposition with respect to initially taken H_2O_2, error was measured based on obtained mean value; [b]Different conditions are used here (conditions: MeOH = 20 g, catalyst = 0.3 g, 50 % aq. H_2O_2 = 8 g, 1 atm. pressure, 35 °C, 1400 rpm, 2h stirring)

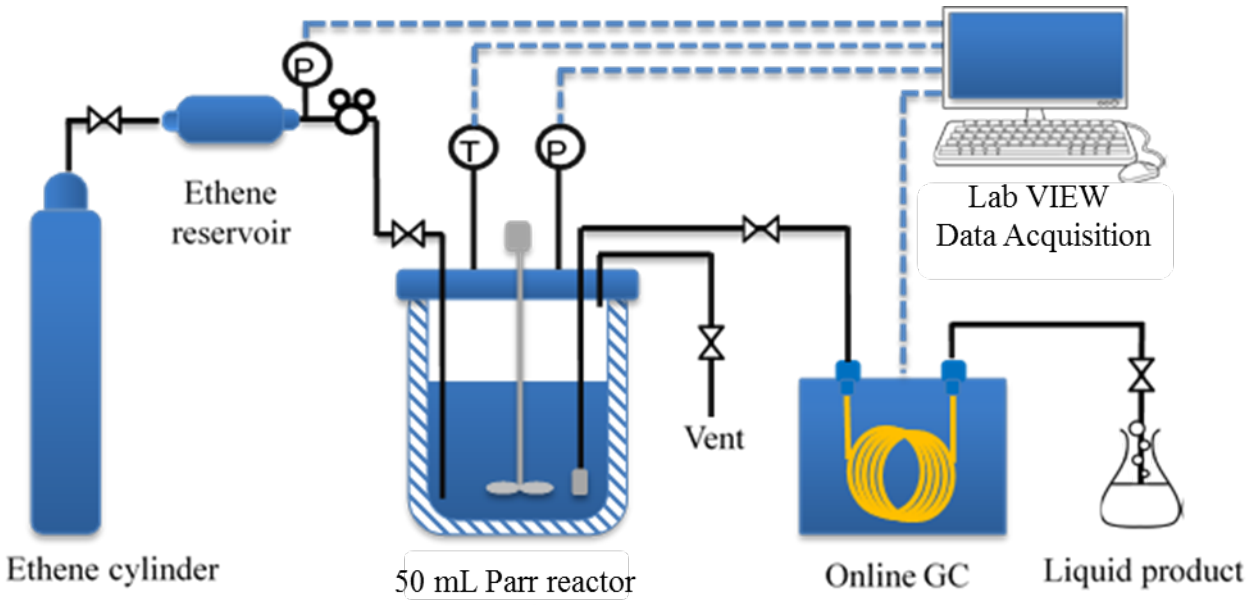

Figure S1. Schematic of experimental unit

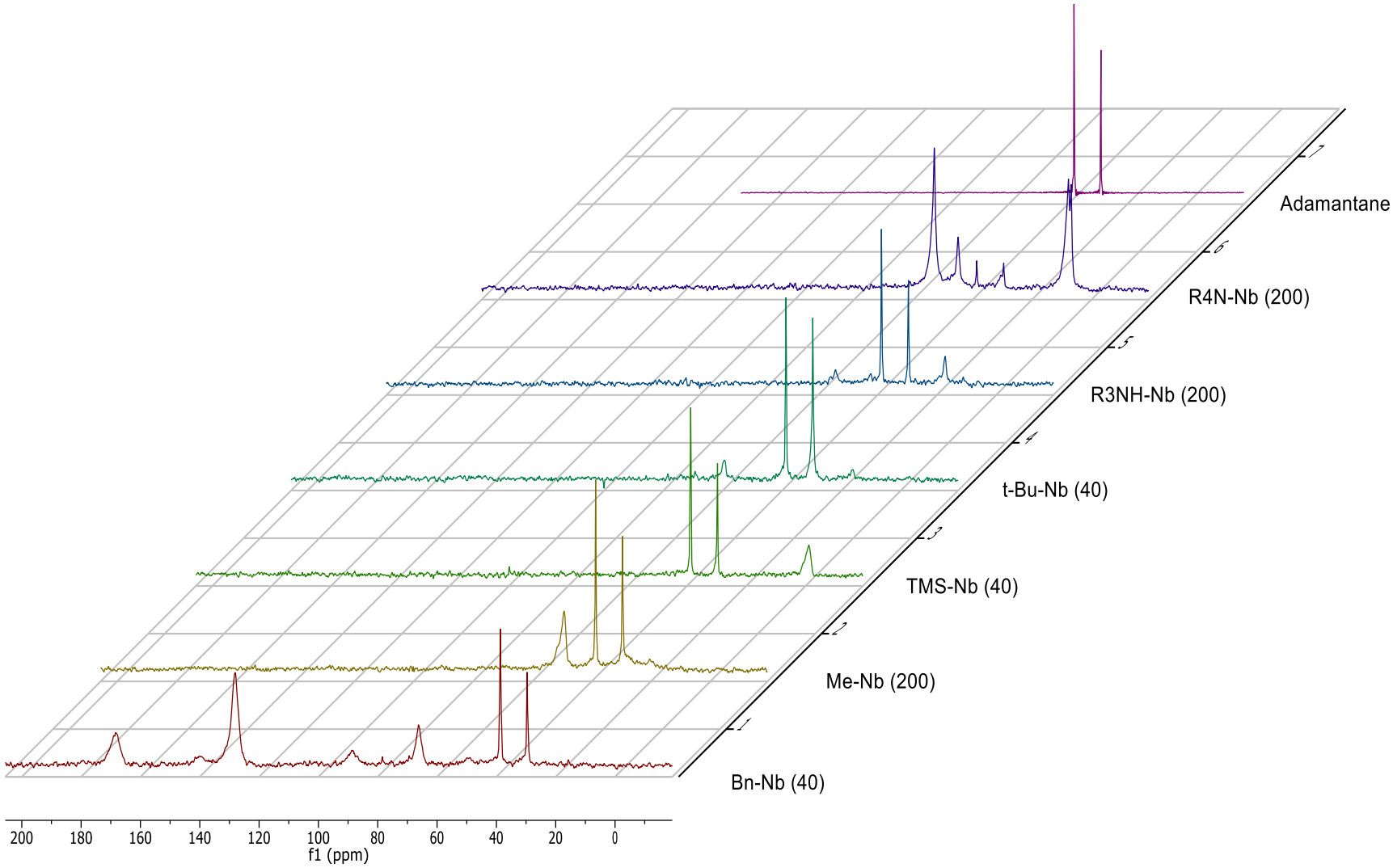

Figure S2: ^{13}C MAS-NMR spectra for parent and capped Nb-TUD-1 catalysts

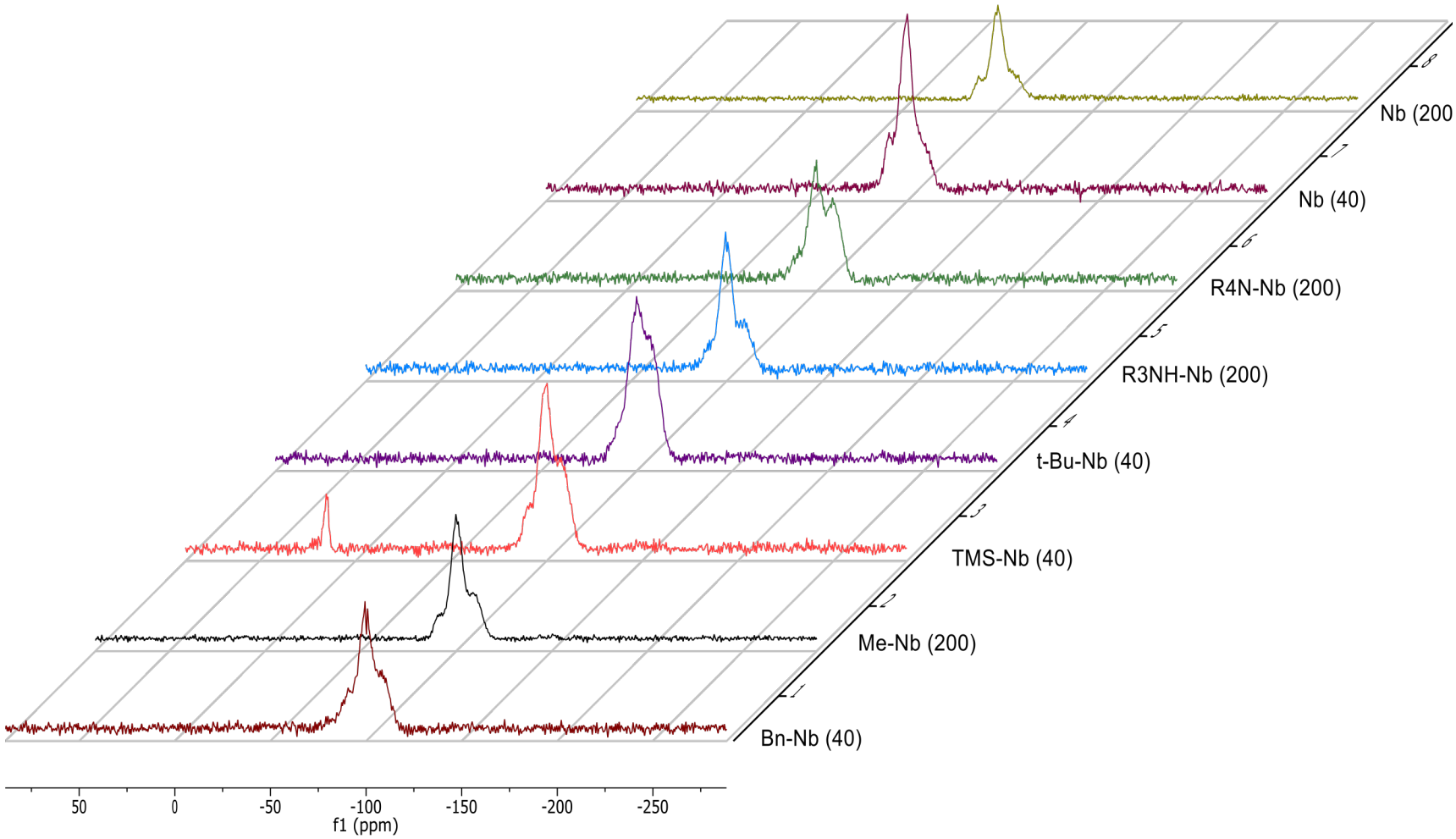

Figure S3: ^{29}Si MAS NMR spectra for parent and capped Nb-TUD-1 catalysts

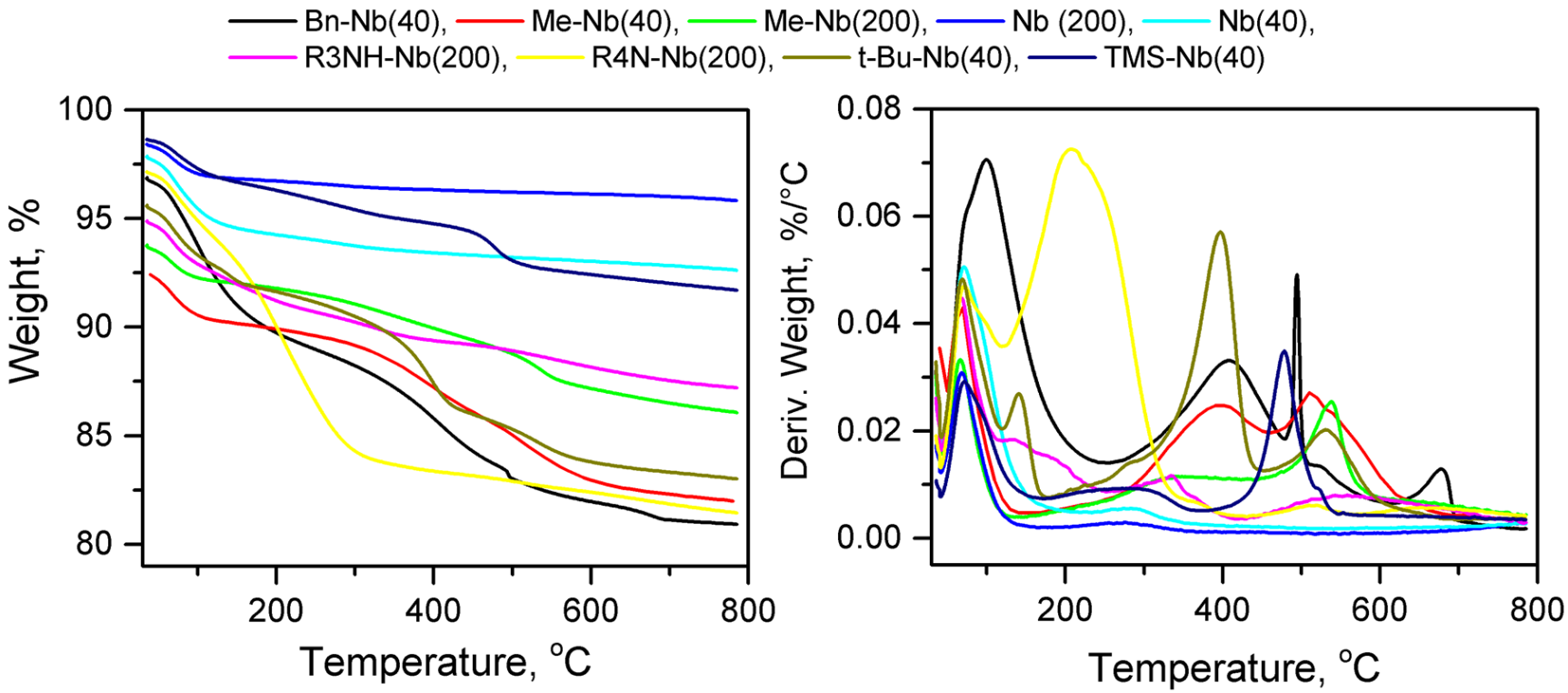

Figure S4. TG (left) and DTA (right) profiles for uncapped and capped Nb-TUD-1 catalysts

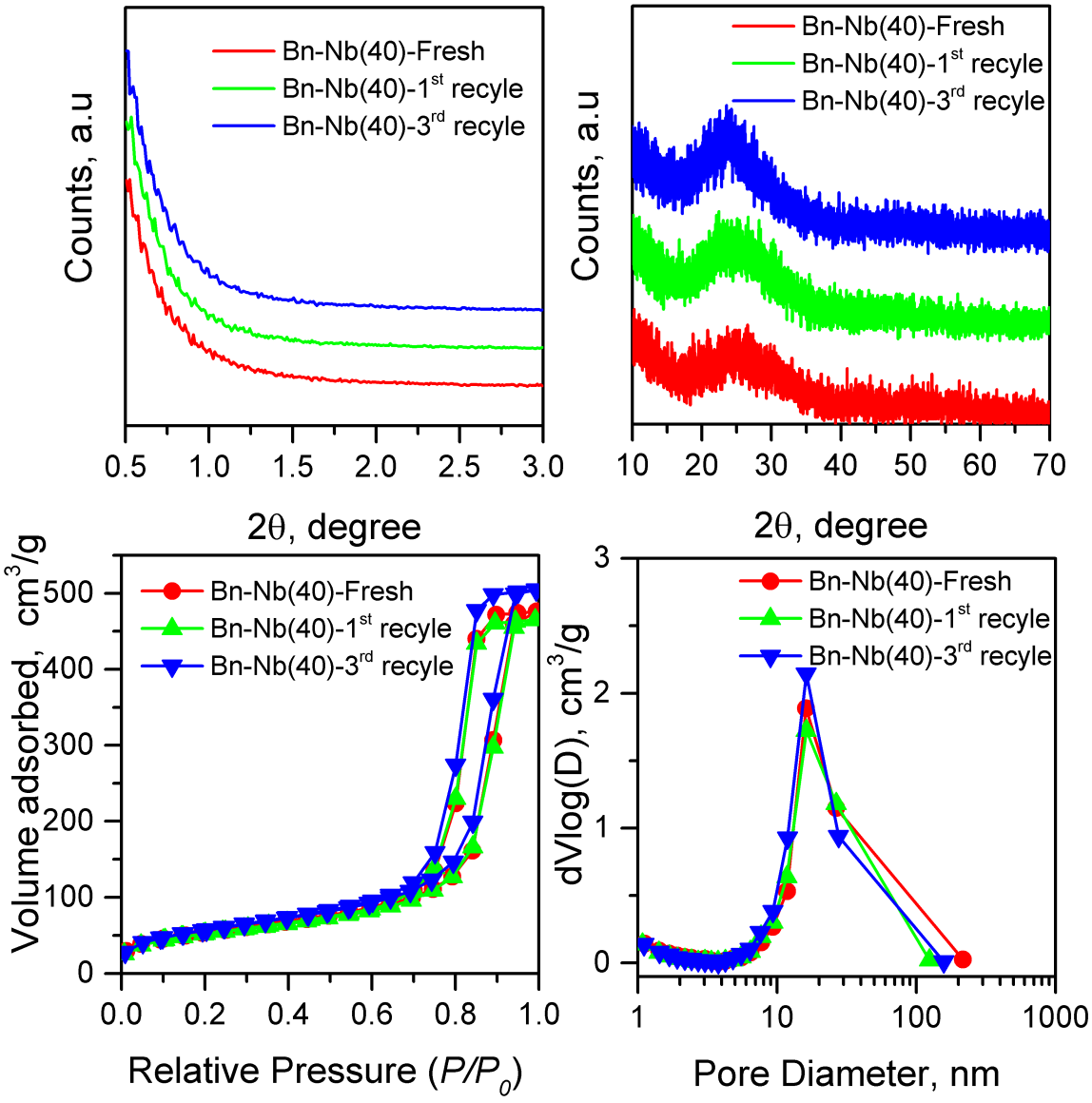

Figure S5. SAXS (top left), wide angle XRD (top right), nitrogen isotherm (bottom left) and pore size distributions (bottom right) of fresh Bn(40) and recycled catalysts