Supplemental Information for:

Fast MAS ^{1}H NMR Study of Water Adsorption and Dissociation on the (100) Surface of Ceria Nanocubes: A Fully Hydroxylated, Hydrophobic Ceria Surface

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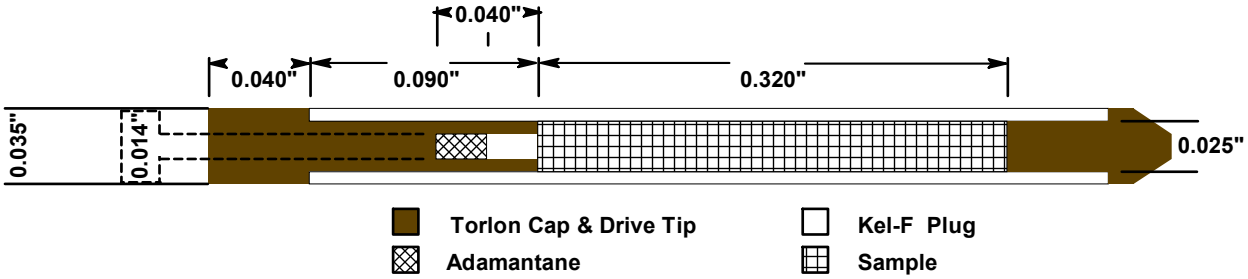


Figure S1. Schematic design of the rotor assembly with the adamantane packed cap used in quantitative experiments using a 1.2mm pencil style rotor.

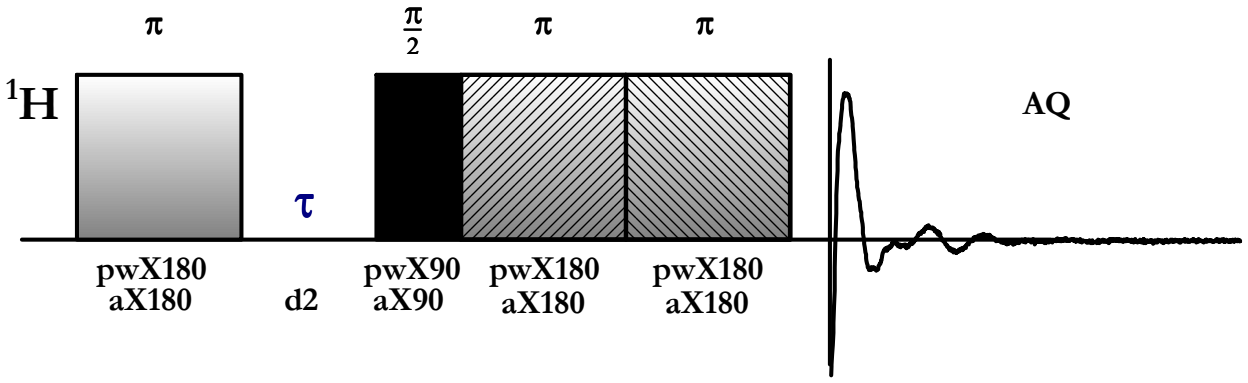


Figure S2a. DEPTH filter adaptation of the standard inversion-recovery pulse sequence for measuring T_1 with background suppression (twopuldpth).

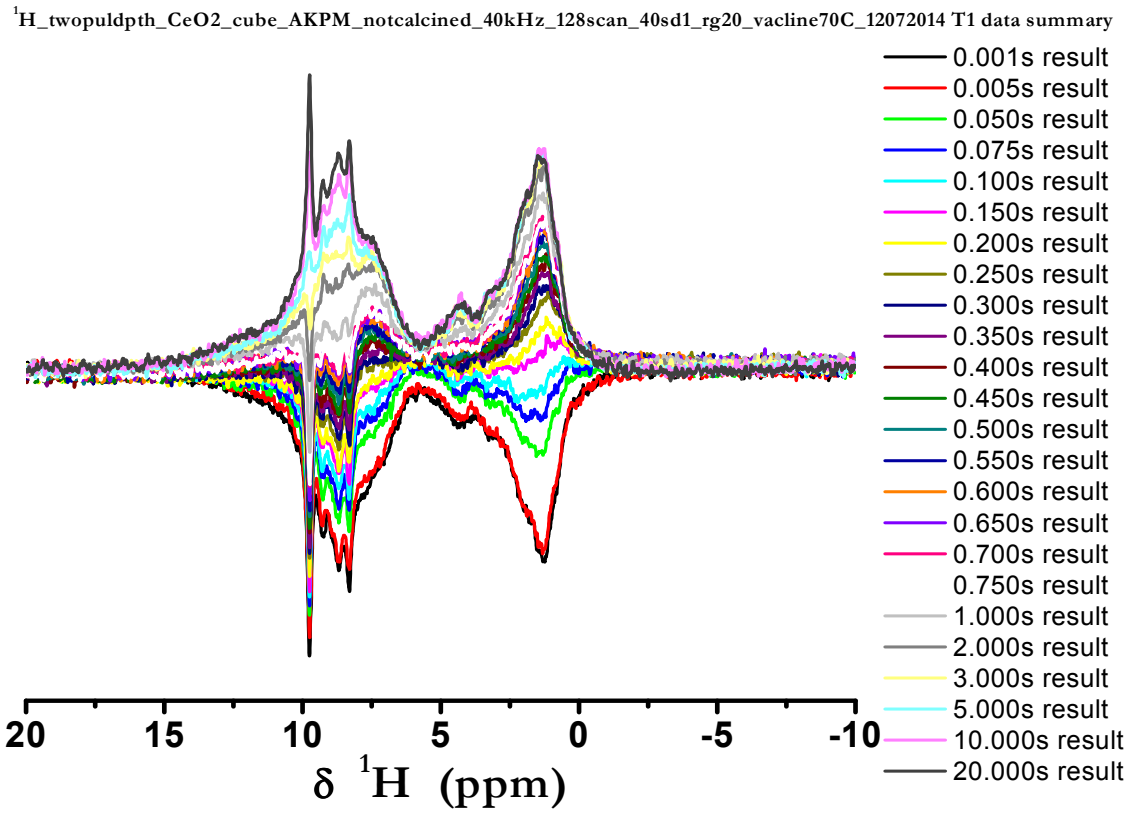


Figure S2b. T_1 inversion-recovery spectra of non-calcined ceria nanocubes using the twopuldpth sequence above. The τ-value list is given in the figure. A background T_1 inversion-recovery data set was collected using an empty rotor over the same time scale and each spectrum in the plot above has had the remaining suppressed background removed for more accurate determination of the relaxation rates.

Figures S3-S7, Table S1 and accompanying text: Spin Counting: Surface coverage analysis for evacuated and heated non-calcined ceria nanocubes.

All quantitative spin counting experiments employ one-pulse experiments. The recycle delay was 480 s in benzoic acid calibration experiments to accommodate the 110 s T_1 of the acid proton of benzoic acid-*d5*. The ceria samples were acquired using a 40 s recycle delay. The shorter recycle delay does not change the area of the adamantane reference or background signals relative to the calibration runs with the long recycle delay, and is 4 times the longest T_1 of the hydroxylic species measured in the ceria nanocubes.

Figure S3 shows the one pulse benzoic acid-d5/ adamantane spectrum and its deconvolution into its components. Two overlapping lines were used in order to fit accurately the area of the acid proton resonance of benzoic acid. The area sum of these lines (13 ppm) is used in the calculations. The protonated aromatic resonances (8.2, 7.2 and 6.2 ppm) that arise from the ca. 0.5%H in the deuterated ring are also fit, as is the adamantane resonance (1.78 ppm), all with single component lines. The remaining, residual area is identified with six additional lines necessary to result in a flat baseline. These resonances are the background signals, identified here and in empty rotor experiments (not shown). The agreement in position and relative intensity of these lines in these experiments justifies their use in subtraction experiments for ceria samples. The benzoic acid, adamantane and probe background signal data from the deconvolution are tabulated under the spectra in Figure S3. The benzoic acid and adamantane area ratio along with the measured mass of benzoic acid in the rotor (1.7 mg, 1.337×10^{-5} mol) yield the effective adamantane mass of 4.41 μg (3.237×10^{-8} mol) in the adamcap. The adamcap used in these calibration experiments was used in the subsequent experiments on the ceria nanocubes.

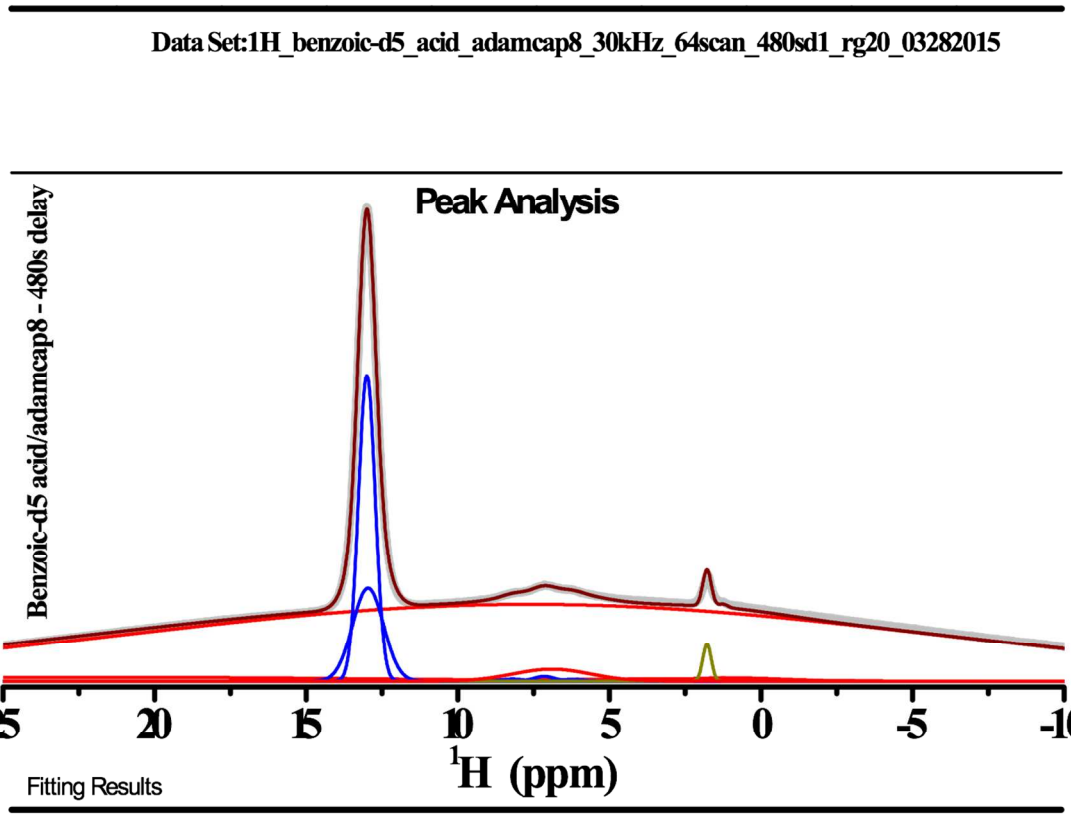
Figures S4-S7 show ceria spectra recorded with the adamcap for the as-received ceria nanocubes, (Figure S4, cube 1 in Table S1), the as-received ceria sample evacuated at room temperature (Figure S5, cube 2 in Table S1), evacuated at 100 ˚C (Figure S6, cube 3 data in Table S1), and evacuated at 160 ˚C (Figure S7, cube 4 in Table S1). Data for the sample evacuated at 200 ˚C is also given (cube 5 in Table S1). The deconvolution analyses are tabulated under the spectra. Derived quantities from the area data are collected in Table S1. The calculations use the following values (see Table S1 footnotes)

Effective adamantane amount in adamcap: 3.237×10^{-8} moles

Surface area of a water molecule: 11.65×10^{-20} m^2/H_2O (See Table 1 in paper)

Surface area of an –OH function on the ceria (100) surface: 7.317×10^{-20} m^2/-OH (See Table 1 in paper)

The surface area determined on calcined ceria nanocubes in this work is 17 m^2/g. The spin counting experiments used 3.6 mg of as-received, non-calcined ceria nanocubes with an assumed surface area of 0.0612 m^2).

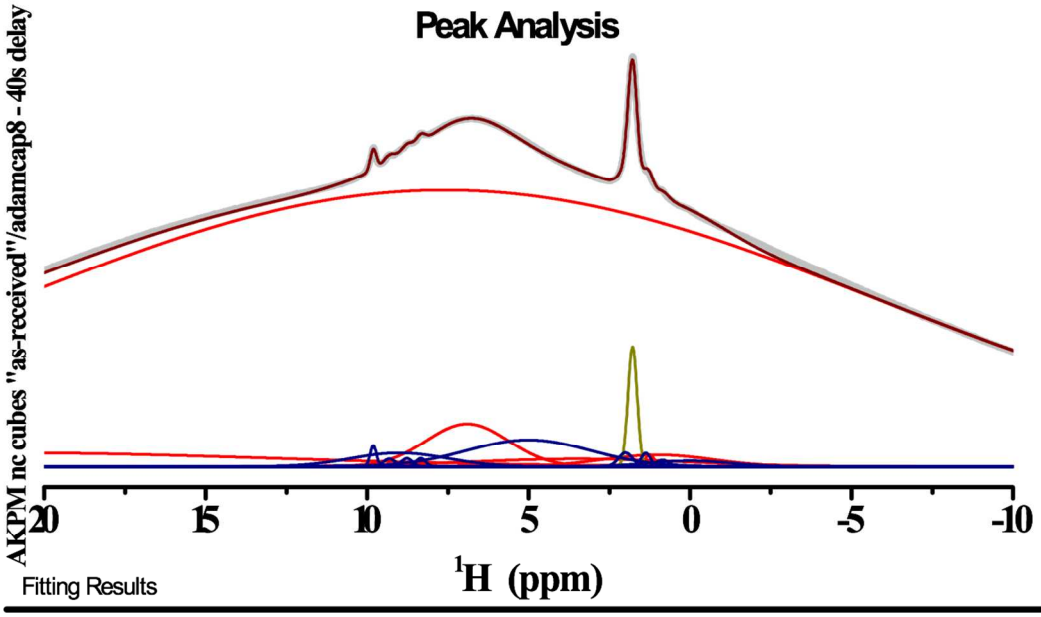


Fitting Results

Peak	Peak Type	Area Intg	FWHM	Center Grvty	Area IntgP
1.	Background	-0.17392	20	21.5	-2.67067
2.	Background	-5.44835	31.5	7.6	-83.66449
3.	Background	-0.03831	8	3.5	-0.58825
4.	Background	-0.00255	0.35	1.25	-0.03923
5.	Background	-0.02935	4	1	-0.45069
6.	Benzoic Acid	-0.2512	12	12.96	-3.85735
7.	Benzoic Acid	-0.44573	0.65	13	-6.84463
8.	Benzoic Acid	-0.00378	0.8	8.2	-0.05799
9.	Benzoic Acid	-0.0085	0.8	7.15	-0.1306
10.	Benzoic Acid	-0.00333	0.8	6.2	-0.05119
11.	Adamantane	-0.027	0.33	1.78	-0.41461
12.	Background	-0.08012	3	6.9	-1.23032

Figure S3. Calibration spectra for adamcap 8. The top spectrum, of benzoic acid-d5 packed in the rotor and adamantane in the adamcap, is the experimental spectrum. Deconvolution spectra and component analysis for these resonances and for background signals from remote probe parts is listed below the spectrum.

Data Set:1H_CeO2_cube_AKPM_notcalcined_adamcap8_30kHz_64scan_40sd1_rg20_0402015_fit

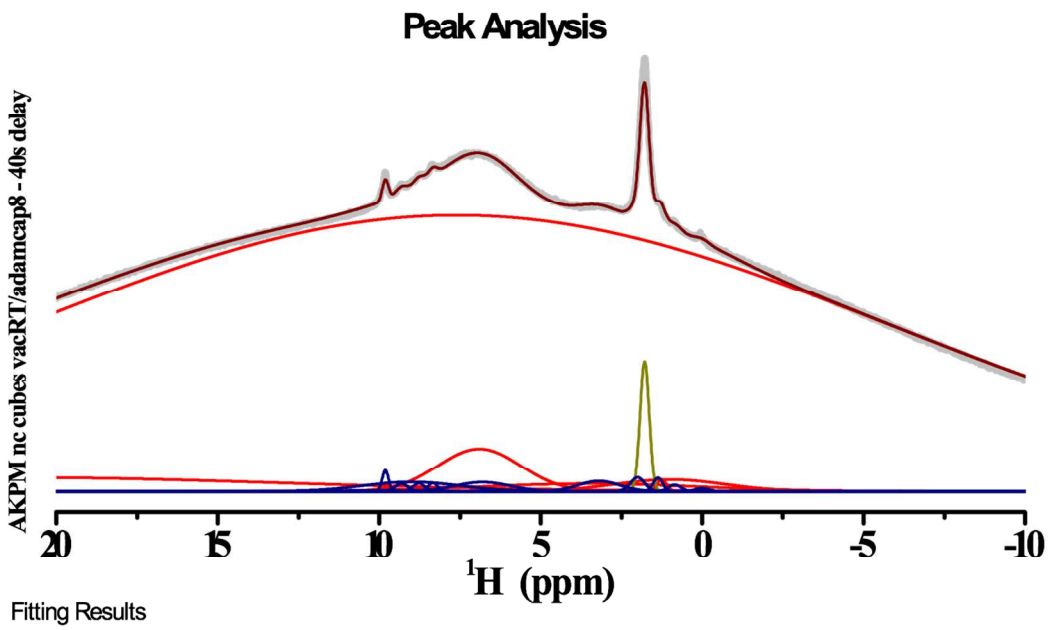


Fitting Results

Peak	Type	Area Intg	FWHM	Center Grvty	Area IntgP
-1	Background	-0.17392	20	21.5	-2.93146
-2	Background	-5.44835	31.5	7.6	-91.83439
-3	Background	-0.03831	8	3.5	-0.64569
-4	Background	-0.00255	0.35	1.25	-0.04306
-5	Background	-0.02935	4	1	-0.4947
-6	Adamantane	-0.02476	0.33	1.78	-0.41732
-7	Background	-0.08012	3	6.9	-1.35046
-8	AKPM nc cubes	-0.00125	3	10.2	-0.02107
-9	AKPM nc cubes	-0.00296	0.22474	9.81	-0.04991
-10	AKPM nc cubes	-0.00217	0.44546	9.31	-0.03653
-11	AKPM nc cubes	-0.00206	0.40363	8.77	-0.03476
-12	AKPM nc cubes	-0.00176	0.33677	8.34	-0.02959
-13	AKPM nc cubes	-0.03	3.5	9	-0.50566
-14	AKPM nc cubes	-0.07522	4.5	5	-1.26781
-15	AKPM nc cubes	0	0	4.7	0
-16	AKPM nc cubes	-0.00446	0.51431	2	-0.0751
-17	AKPM nc cubes	-0.00288	0.34	1.37	-0.0486
-18	AKPM nc cubes	-0.00183	0.45	0.85	-0.03086
-19	AKPM nc cubes	-0.01086	3	0	-0.18302

Figure S4. The spectrum of as-received, non-calcined nanocubes recorded with adamcap8. Deconvolution spectra and component analysis are below. Note the position and intensity of background signals are unchanged from Figure S3.

Data Set:1H_CeO2_cube_AKPM_notcalcined_adamcap8_30kHz_64scan_40sd1_rg20_vacquartzRT_04022015_fit

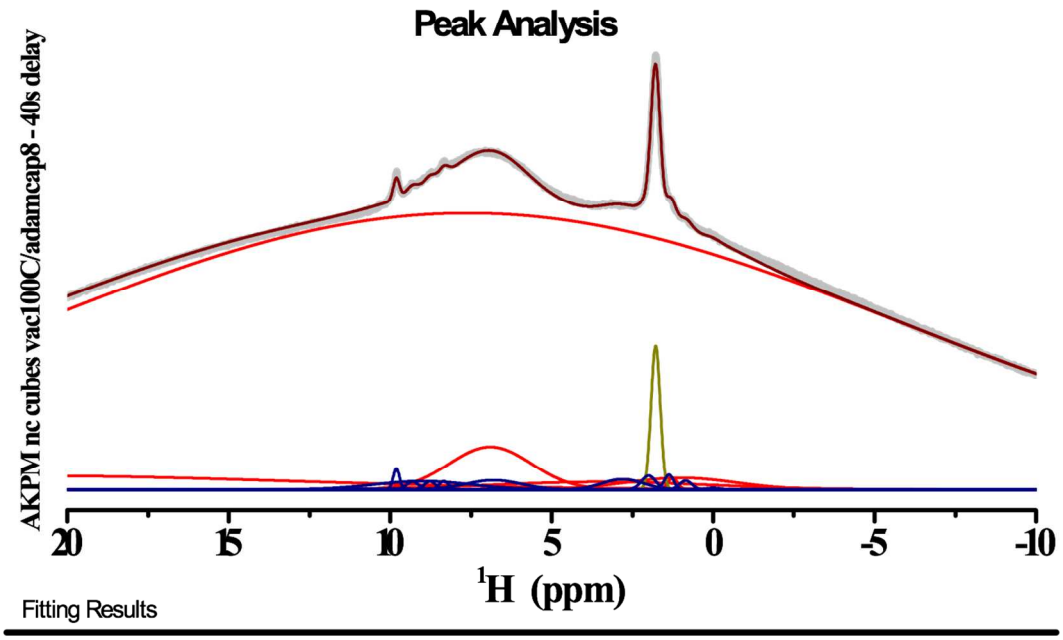


Fitting Results

Peak	Type	Area Intg	FWHM	Center Grvty	Area IntgP
-1	Background	-0.17392	20	21.5	-2.96706
-2	Background	-5.44835	31.5	7.6	-92.94954
-3	Background	-0.03831	8	3.5	-0.65353
-4	Background	-0.00255	0.35	1.25	-0.04358
-5	Background	-0.02935	4	1	-0.50071
-6	Adamantane	-0.027	0.33	1.78	-0.46062
-7	Background	-0.08012	3	6.9	-1.36686
-8	AKPM nc cubes	-0.00125	3	10.2	-0.02133
-9	AKPM nc cubes	-0.00296	0.22474	9.81	-0.0505
-10	AKPM nc cubes	-0.00217	0.44546	9.31	-0.03702
-11	AKPM nc cubes	-0.00206	0.40363	8.77	-0.03514
-12	AKPM nc cubes	-0.00176	0.33677	8.34	-0.03003
-13	AKPM nc cubes	-0.02062	3.5	9	-0.35175
-14	AKPM nc cubes	-0.01148	2	6.8	-0.19587
-15	AKPM nc cubes	-0.00965	1.5	3.2	-0.16456
-16	AKPM nc cubes	-0.00446	0.51431	2	-0.07609
-17	AKPM nc cubes	-0.00288	0.34	1.37	-0.04913
-18	AKPM nc cubes	-0.00183	0.45	0.85	-0.03122
-19	AKPM nc cubes	-9.1E-4	0.48	0	-0.01548

Figure S5. The spectrum of as-received, non-calcined nanocubes evacuated under high vacuum at room temperature (2h) recorded with adamcap8. Deconvolution spectra and component analysis are below.

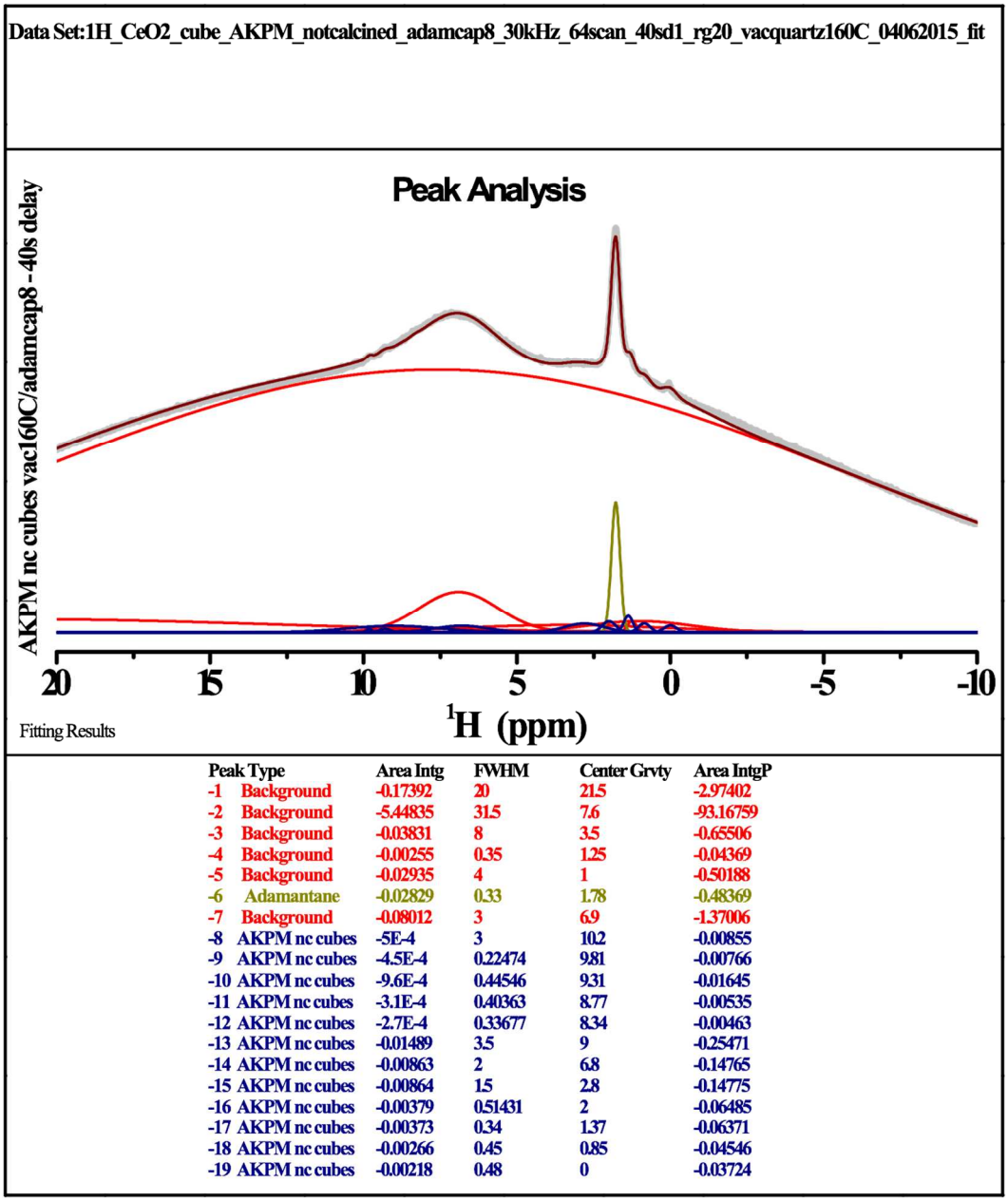
Data Set:1H_CeO2_cube_AKPM_notcalcined_adamcap8_30kHz_64scan_40sd1_rg20_vacquartz100C_04032015_fit



Fitting Results

Peak	Type	Area Intg	FWHM	Center Grvty	Area IntgP
-1	Background	-0.17392	20	21.5	-2.96624
-2	Background	-5.44835	31.5	7.6	-92.92413
-3	Background	-0.03831	8	3.5	-0.65335
-4	Background	-0.00255	0.35	1.25	-0.04357
-5	Background	-0.02935	4	1	-0.50057
-6	Adamantane	-0.02974	0.33	1.78	-0.50718
-7	Background	-0.08012	3	6.9	-1.36648
-8	AKPM nc cubes	-0.00125	3	10.2	-0.02132
-9	AKPM nc cubes	-0.00296	0.22474	9.81	-0.05048
-10	AKPM nc cubes	-0.00217	0.44546	9.31	-0.03701
-11	AKPM nc cubes	-0.00206	0.40363	8.77	-0.03513
-12	AKPM nc cubes	-0.00176	0.33677	8.34	-0.03002
-13	AKPM nc cubes	-0.01853	3.5	9	-0.31598
-14	AKPM nc cubes	-0.01177	2	6.8	-0.20072
-15	AKPM nc cubes	-0.00977	1.5	2.8	-0.16671
-16	AKPM nc cubes	-0.00446	0.51431	2	-0.07607
-17	AKPM nc cubes	-0.00316	0.34	1.37	-0.05382
-18	AKPM nc cubes	-0.00252	0.45	0.85	-0.043
-19	AKPM nc cubes	-4.8E-4	0.48	0	-0.00819

Figure S6. The spectrum of as-received, non-calcined nanocubes evacuated under high vacuum at 100 °C (2h) recorded with adamcap8. Deconvolution spectra and component analysis are below.



	Peak Type	Area Intg	FWHM	Center Grvty	Area IntgP
-1	Background	-0.17392	20	21.5	-2.97402
-2	Background	-5.44835	31.5	7.6	-93.16759
-3	Background	-0.03831	8	3.5	-0.65506
-4	Background	-0.00255	0.35	1.25	-0.04369
-5	Background	-0.02935	4	1	-0.50188
-6	Adamantane	-0.02829	0.33	1.78	-0.48369
-7	Background	-0.08012	3	6.9	-1.37006
-8	AKPM nc cubes	-5E-4	3	10.2	-0.00855
-9	AKPM nc cubes	-4.5E-4	0.22474	9.81	-0.00766
-10	AKPM nc cubes	-9.6E-4	0.44546	9.31	-0.01645
-11	AKPM nc cubes	-3.1E-4	0.40363	8.77	-0.00535
-12	AKPM nc cubes	-2.7E-4	0.33677	8.34	-0.00463
-13	AKPM nc cubes	-0.01489	3.5	9	-0.25471
-14	AKPM nc cubes	-0.00863	2	6.8	-0.14765
-15	AKPM nc cubes	-0.00864	1.5	2.8	-0.14775
-16	AKPM nc cubes	-0.00379	0.51431	2	-0.06485
-17	AKPM nc cubes	-0.00373	0.34	1.37	-0.06371
-18	AKPM nc cubes	-0.00266	0.45	0.85	-0.04546
-19	AKPM nc cubes	-0.00218	0.48	0	-0.03724

Figure S7. The spectrum of as-received, non-calcined nanocubes evacuated under high vacuum at 160 °C (2h) recorded with adamcap8. Deconvolution spectra and component analysis are below.

Table S1. Water and –OH Surface Area Coverage Calculations for Non-calcined Ceria Nanocubes

Column	1[a]	2[a]	3[a]	4[b]	5[c]	6[d]	7[e]	8[f]	9[g]	10[h]	11[i]
Data	1[j] area	H_2O area	-OH area	H_2O/1 mole ratio	-OH/1 mole ratio	H_2O moles	-OH moles	H_2O m^2	-OH m^2	H_2O % ML	-OH % ML
Cube 1	0.0248	0.0752	0.0602	24.296	40.259	0.7865	1.3031	0.0552	0.057	90	94
Cube 2	0.027	0.0115	0.0496	3.4015	29.416	0.1101	0.9694	0.0077	0.0427	13	70
Cube 3	0.0297	0.0118	0.0486	3.1657	26.168	0.1025	0.8471	0.0072	0.0373	12	61
Cube 4	0.0283	0.0086	0.0362	2.4404	20.474	0.0790	0.6627	0.0055	0.0293	9	48
Cube 5	0.027		0.0376		22.252		0.7203		0.0317	0	52

a. Area sums from spectral deconvolution data.
b. 0ne-half the water area divided by one-sixteenth the adamantane area.
c. –OH area divided by one-sixteenth the adamantane area.
d. Column 4 times the effective moles of adamantane.
e. Column 5 times the effective moles of adamantane.
f. Column 6 times Avogadro's number times the generic water surface area.
g. Column 7 times Avogadro's number times –OH surface area.
h. 100 times Column 8 divided by the ceria nanocube surface area.
i. 100 times Column 9 divided by the ceria nanocube surface area.
j. 1 represents adamantane. The adamantane reference area is reproducible ±10% and indicates the magnitude of the error from the integration and deconvolution steps. Overall error is considered to be on the order of ± 20 %.

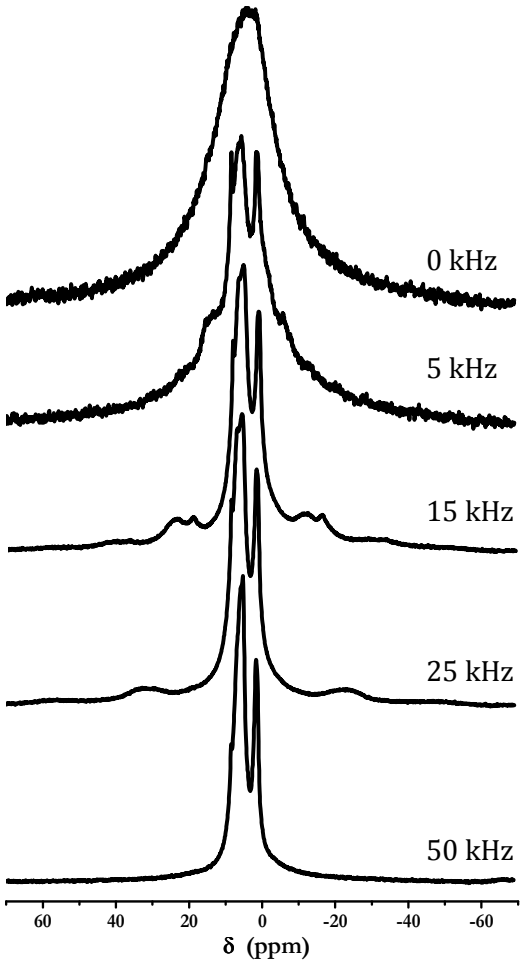


Figure S8. Ceria commercial sample spectra measured at different MAS speeds.

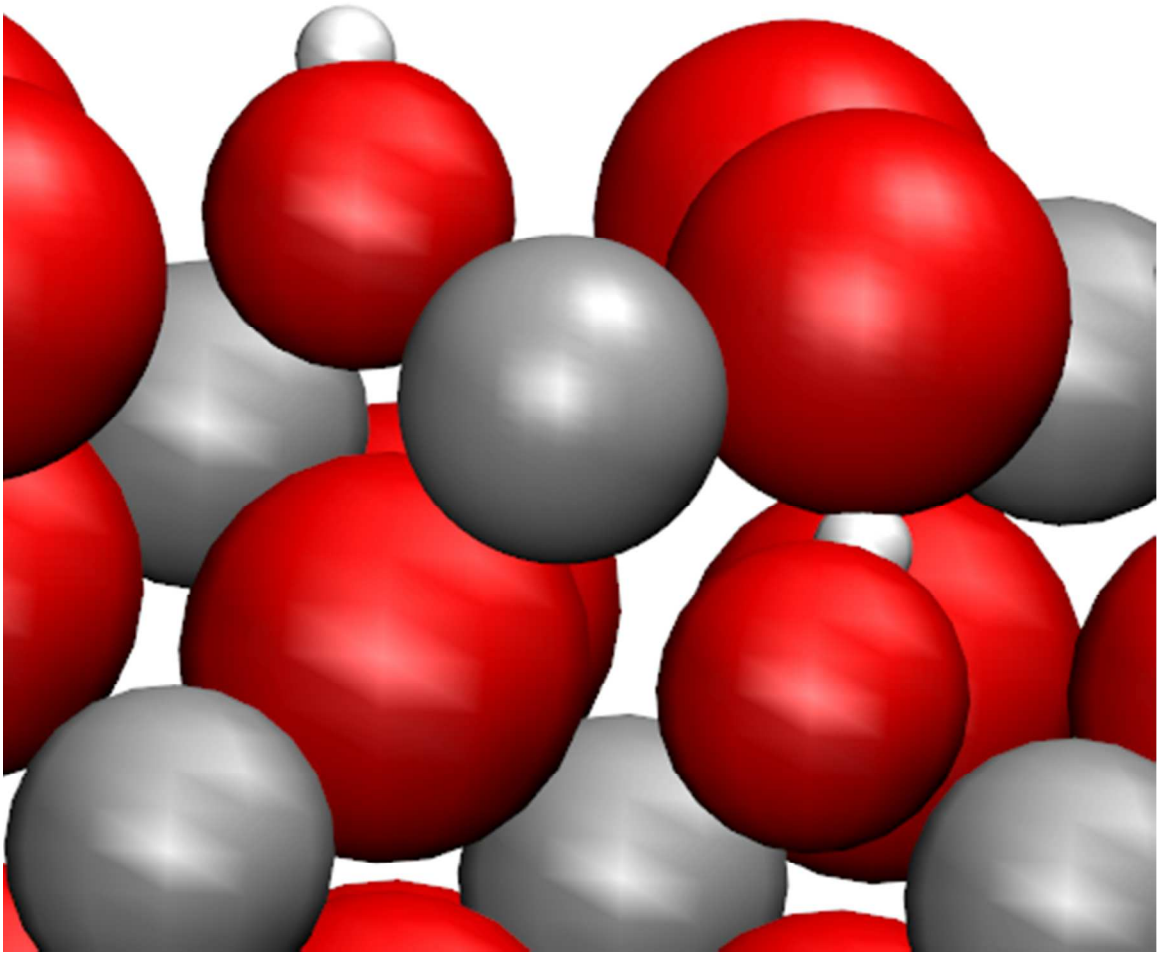


Figure S9. Possible subsurface -OH configuration on ceria, with the –OH bound in the third atomic layer.

The full citation for reference (70) in the paper:

(70) Wang, M.; Wu, X.-P.; Zheng, S.; Zhao, L.; Li, L.; Shen, L.; Gao, Y.; Xue, N.; Guo, X.; Huang, W.; Gan, Z.; Blanc, F.; Yu, Z.; Ke, X.; Ding, W.; Gong, X.-Q.; Grey, C. P.; Peng, L. Identification of Different Oxygen Species in Oxide Nanostructures with ^{17}O Solid-State NMR Spectroscopy, *Sci. Adv*. **2015**, 1:e1400133.