Supporting Information for:

Selective ^{17}O-Labeling of Silica

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Materials and Methods

Synthesis

Silica selectively ^{17}O-enriched at its silanols. Davisil silica gel, grade 646, 35-60 mesh, pore size 150 Å, was purchased from Sigma-Aldrich. Approximately 12 mg of silica was added to a borosilicate tube that was connected to a Schlenk line through a Teflon valve fitting. The silica material was dried at 25 °C for 2 hours under dynamic vacuum to a pressure of c.a. 20 mTorr. Then, 39.3% by weight ^{17}O-enriched water (Cortecnet) was added to the tube until the silica material surpassed the incipient wetness point. The mixture was left to react at room temperature overnight under a sealed atmosphere. The sample was subsequently dried once more at room temperature under dynamic vacuum.

Uniformly ^{17}O-enriched silica.[1] Approximately 300 mg of the silica gel was dried at 700 °C overnight under dynamic vacuum in a tube furnace using the same setup as described in the previous section, albeit with the use of a quartz tube. Following this, the tube was inserted into a wet box and 100 µL of 90% ^{17}O-enriched water (Cortecnet) was added to the tube. The mixture was left to react at room temperature for 6 hours. This procedure was repeated for a total of 5 times after which the sample was dried once more at 700 °C under dynamic vacuum. *Upon being* exposed to air in a fume hood over 7 days, this material was found to have been ^{17}O-depleted in silanols.

Acidic stock solutions. Concentrated hydrochloric acid was purchased from Fisher Scientific. 1 µL of the acid was diluted to 10 mL using deionized water to produce a stock solution with a pH of 1. Solutions of pH 3 and 5 were obtained by further serial dilutions of the stock solution.

Basic stock solution. Sodium hydroxide pellets were purchased from Fisher Scientific. 0.8 mg of NaOH was dissolved in deionized water to a volume of 25 mL to produce a stock solution with a pH of 11. A solution with a pH of 9 was obtained by serial dilutions.

Solid State NMR Spectroscopy

Solid-state NMR experiments were performed using either a Bruker AVANCE NEO 600 MHz NMR spectrometer equipped with a Bruker 4 mm MAS probe or a Bruker AVANCE III 600 MHz NMR spectrometer equipped with a Varian 3.2 mm MAS probe. In all cases the MAS frequency was set to 10 kHz.

In situ NMR. ~10 mg of ^{17}O-enriched silica was added to a high-resolution (HR)MAS insert for a Bruker 4 mm MAS rotor. ~10 mg of an acid/base stock solution was subsequently added to the insert. NMR experiments were conducted using a Bloch decay sequence with a 4.5 µs ^{17}O excitation pulse. Each spectrum was acquired in 256 scans, with the recycle delay being set to 1 s, leading to a 4.26 min time resolution. The data were fitted to a monoexponential buildup (equation S1), which assumed first-order kinetics. The fitted rate constants (k) are given in **Table S1**.

$$\left[{}^{17}OH_2\right] = \left[{}^{17}OH_2\right]_{max}(1 - exp(-kt)) \quad \text{(S1)}$$

Table S1. pH dependence of the hydroxyl exchange rates.

pH	k (h^{-1})
3	2.09 ± 0.15
5	2.84 ± 0.15
7	3.37 ± 0.18
9	3.06 ± 0.19

^{17}O Hahn echo experiments were performed on the solid, selectively ^{17}O-enriched, silica materials using a rotor-synchronized echo delay and 10 and 20 μs central transition-selective 90 and 180° pulses. Each subspectrum was acquired in 65536 scans with a 1 s recycle delay.

^{17}O Multiple-quantum MAS (MQMAS) experiments were performed using a 3.2 mm MAS probe using the soft-pulse added mixing (SPAM) trick.[2] The excitation, reconversion, and detection pulses lasted 2.5, 1.75, and 10 μs, respectively. The spectra were acquired in 32 t_1 increments of 100 μs, each consisting of 3900 scans with a 0.58 s recycle delay.

Density Functional Theory Calculations

Density functional theory (DFT) calculations of the hydroxyl exchange mechanism were performed using the Amsterdam Density Functional (ADF, ver. 2022.190) program. All calculations were performed at the PBE0/TZ2P level of theory.[3-4] Structural models of the amorphous silica surface were adapted from the periodic models developed by Ugliengo and co-workers.[5,6] Briefly, an exposed surface silanol site was selected and the three nearest silicon shells were kept and terminated with hydrogen atoms. The third silicon shell was kept fixed in the molecular models during geometry and transition state optimizations to emulate its bonding to an extended solid silica material. Solvent effects were treated using the COSMO method.[7]

Geometry optimized structure of amorphous silica with a water molecule

Si	1.35974840528934	9.50981302211117	14.63866123321290
Si	3.77284916579171	7.96701435881767	15.45889007647049
Si	5.86518148074933	6.75607932818152	17.14117729660554
O	9.51933477232717	6.15213812059925	15.42653034608497
H	6.17542471620944	9.24456632045127	13.20779997855927
O	7.50707506129913	7.40864059657136	14.26175314287878
Si	10.27178263064913	10.13155589688979	15.57674945352447
H	6.00550879051101	2.17500734787129	12.64515641384782
H	7.40498201453386	4.12554853069015	12.27498757908644
H	6.25750900658150	6.08476727039397	19.24777692226438
H	10.12457651992963	4.67913692150856	13.41719653551045
Si	8.48149350263208	7.38636556936015	15.55860449225894
O	9.27578463615369	8.78657336279655	15.75368810649643
O	7.41366449858395	7.11255414803931	16.78781476556760
Si	10.55481852132075	5.00997110753212	14.79334324943344
H	6.11788631877358	6.97677594086664	12.25589494749889
O	5.67795017638841	6.67318755615197	18.75635359512132
O	2.95940009458655	9.33727271243118	15.16355023280651
Si	4.03917739038052	1.29144474484655	16.01095097142068
Si	2.09042220734157	5.59544407595283	14.81417196450926

O	3.27521184572503	4.48411978595374	14.98400898504790
Si	4.79736969098295	4.21226051335154	15.46763484470327
O	2.58398160706788	6.87845021795083	15.71478600349305
O	5.35838416975932	5.36426828516630	16.46801062474892
Si	6.76269705122055	3.26943517595158	13.29592057157081
O	5.74790791462967	4.21426789910924	14.16592187577592
O	4.80783276310743	2.75763454205151	16.18447670082796
Si	6.13838752904491	7.79162672460470	13.48354189265312
O	4.70644607220531	7.48788029030659	14.22154692566553
O	4.80417127621608	7.94650058178802	16.72615583051773
H	1.23452201480622	10.89696307897506	14.15172868855225
H	11.92821620768982	5.55749341320152	14.78855019402689
H	10.47796508091073	3.81134504822273	15.65580417750280
H	7.79247836673574	2.69017962554174	14.19197426922542
H	9.83443093617243	10.88621643236128	14.38221046589774
H	11.66851841455112	9.67089812019829	15.42000447976322
H	10.12596212236555	10.95310467507667	16.79684952465810
H	1.10269658625990	8.53967774520274	13.55178087682973
H	0.44935487445847	9.25993682855811	15.77662722146114
H	1.96327145042419	5.97797204595677	13.39626744758619
H	0.83589182717806	5.09279788774228	15.39450338983088
H	4.70102461973991	0.34674320203452	16.93440111376833
H	2.60632683023241	1.43991599922371	16.35337112631325
H	4.17736987597081	0.83309327151665	14.60857071390178
O	2.67782344781875	6.47583594111423	18.86187286291145
H	2.54181246462278	6.59802462150113	17.91536027461083
H	3.63343983260220	6.55969622987179	18.98596149932540

Transition state for hydroxyl exchange

Si	1.35974840528934	9.50981302211117	14.63866123321290
Si	3.76861046660311	7.98766440696629	15.45642295838416
Si	5.77892588052292	6.67793457426478	17.19906979347909
O	9.51354548517458	6.15043401367890	15.42069055702731
H	6.18251137182005	9.24833853198859	13.21436118984224
O	7.54749777451494	7.39816159800856	14.18004705469617
Si	10.27178263064913	10.13155589688979	15.57674945352447
H	6.40464573960878	1.85263360123007	13.04319051775999
H	7.07395618811257	3.95054439878645	12.01973231195235
H	7.21967359039104	6.78741642169596	19.14875765079393
H	10.29703701456798	4.84932257842395	13.34410569716247
Si	8.44717161556676	7.37769707930487	15.53933106178367
O	9.26339780610430	8.78580596259595	15.72115239021386
O	7.34167671628283	7.12655403092907	16.70728080881852

Si	10.55481852132075	5.00997110753212	14.79334324943344
H	6.07922038493207	6.99267771290118	12.24367446342413
O	6.32455339021708	7.01366125234076	18.87509899000765
O	2.96462757018275	9.37382703942867	15.16676179863677
Si	4.03917739038052	1.29144474484655	16.01095097142068
Si	2.09042220734157	5.59544407595283	14.81417196450926
O	3.23274289517580	4.48257197498566	15.16502289992914
Si	4.80110955240759	4.17955657579592	15.44224842139265
O	2.54312493653683	6.93207298417027	15.63718609725484
O	5.60681871438024	5.32473073585416	16.25532955209504
Si	6.76269705122055	3.26943517595158	13.29592057157081
O	5.50178243452071	4.04947372257473	13.98675120782535
O	4.85045166154980	2.73497929261767	16.19508910249521
Si	6.13838752904491	7.79162672460470	13.48354189265312
O	4.70573151703096	7.51067992344767	14.21898382474304
O	4.79135699663718	7.93827067712970	16.72551274976745
H	1.19740430881862	10.90796523464327	14.19172020371004
H	11.94564046380760	5.46384697113615	15.01846267730826
H	10.31669012708096	3.73158525690052	15.49845935129697
H	7.94154009168820	3.31926458678075	14.19475494793860
H	9.86122755362873	10.90371176549223	14.38355367250818
H	11.67035561269487	9.66964885845598	15.43882816011032
H	10.11183429626620	10.94438336595456	16.80131962516801
H	1.13178330242599	8.57148305119685	13.51721361704279
H	0.44514877433145	9.20483569647301	15.75984760482535
H	2.06113588285732	5.86000541017438	13.36205683889427
H	0.78865379529901	5.14778770070810	15.33494510989192
H	4.89485988434006	0.23587601047294	16.59165319110917
H	2.74274110232297	1.35971560841138	16.72196837638187
H	3.81134051014237	1.03690820027968	14.56882922519473
O	4.48738960517185	5.96546029840580	18.37189574527345
H	3.66591418780085	6.46542012771779	18.38263864072956
H	5.41760043573138	6.43971785583191	19.17177255254141

Supplementary References

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