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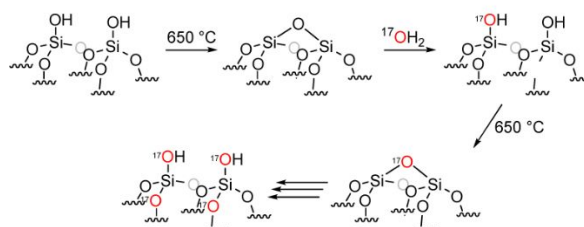
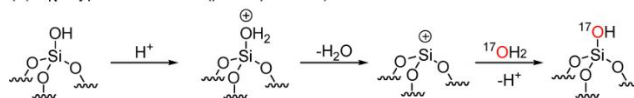
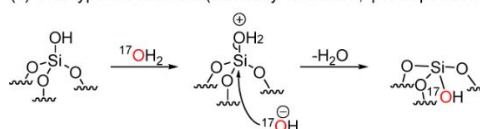
Selective ^{17}O -Labeling of SilicaAmil Agarwal^{a,b}, Marco Mais^b and Frédéric A. Perras^{*b,c}Received 00th January 20xx,
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The addition of $^{17}\text{OH}_2$ to silica at room temperature leads to spontaneous hydroxyl oxygen exchange and the selective isotopic enrichment of silanols, as observed using *in* and *ex situ* ^{17}O NMR. The discovery that silanols are labile alters our understanding of the chemistry of silica surfaces.

Single-site heterogeneous catalysts combine the advantages associated with separations in heterogeneous catalysis and the molecular tunability of homogeneous catalysts.^{1,2} Catalytic sites are often immobilized onto oxide supports, such as silica, through protonolysis reactions, wherein an X-type ligand on the metal is replaced by a silanolate from the surface. With this strategy, high support preparation temperatures can be used to reduce the surface hydroxyl density and prepare relatively isolated sites.^{3–6} These high dehydroxylation temperatures can nevertheless introduce considerable strain in the surface siloxane linkages. As a result, numerous reports have shown alkyl or hydride transfer to silicon to accompany grafting reactions, which leads to the breaking of strained siloxane linkages and the formation of potentially catalytically inert multipodal species.^{7–13} The presumed inert siloxanes have also been implicated in grafting reactions through silanol migration,¹⁴ the formation of paired sites,¹⁵ and thermally-induced reconstructions.^{16,17}

An ideal method to understand these chemical processes would be ^{17}O solid-state NMR (SSNMR) spectroscopy.^{18,19} Metal-bonded oxygen centers are typically well-resolved from silanols and siloxanes, and with proper labeling, would enable the observation of the breaking of siloxane linkages.^{20–25}

(a) Non-selective ^{17}O labelling of silica(b) $\text{S}_{\text{N}}1$ -type mechanism (pH-dependent)(c) $\text{S}_{\text{N}}2$ -type mechanism (sterically-forbidden, pH-dependent)

(d) Hydroxyl exchange via a 4-centered transition state (pH-independent)

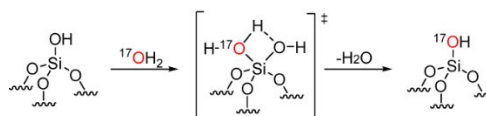


Figure 1. (a) Conventional approach for the uniform surface- ^{17}O -enrichment of silica. (b–d) Potential mechanisms for the selective ^{17}O -labeling of surface silanols: (b) $\text{S}_{\text{N}}1$ -type mechanism, (c) $\text{S}_{\text{N}}2$ -type mechanism, and (d) hydroxyl exchange via a 4-centered transition state. In (a), the three arrows represent repeated de/rehydration cycles.

Unfortunately, preparing site-specifically-labeled silica materials has not yet been demonstrated. The most common approach used to enrich silica with ^{17}O involves repeated thermal dehydroxylation and rehydration of the material using $^{17}\text{OH}_2$.²⁰ This approach leads to the uniform enrichment of all surface sites (silanols and siloxanes, **Figure 1a**). Similarly, oxide materials have been enriched using $^{17}\text{O}_2$ gas at high

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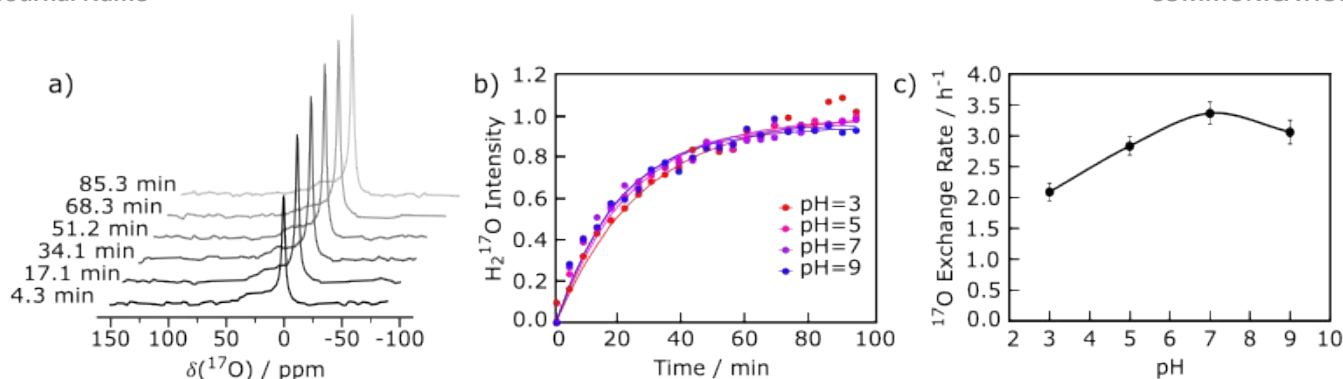


Figure 2. *In situ* MAS NMR study of $^{16}\text{O}/^{17}\text{O}$ isotope exchange between uniformly-enriched Si^{17}O_2 and $^{16}\text{OH}_2$. (a) Example ^{17}O NMR spectra showing the growth of $^{17}\text{OH}_2$ NMR signal intensity in the pH = 7 solution as a function of reaction time. (b) Time dependence of the $^{17}\text{OH}_2$ ^{17}O NMR signal intensity with varying pH values. (c) Plot displaying the independence of the reaction rate with respect to the solution pH. Note that an $\text{S}_{\text{N}}1$ mechanism would have a rate proportional to $[\text{H}_3\text{O}^+]$ (i.e. proportional to 10^{pH}).³⁶

temperatures, which also leads to uniformly-enriched materials.^{26–31} Other recent enrichment methods include mechanochemistry^{32,33} and vapor treatment.³⁴ To date, the recent reports from Ashbrook and co-workers are the only demonstrations of site-specific ^{17}O labeling.³⁵ They showed that the Brønsted acid sites (BAS) in zeolites were more labile than the framework oxygen sites and that BAS-labeled zeolites could be prepared by simple water exposure. This begs the question of whether selectively-labeled silica materials could also be prepared in a similar fashion. Aside from enabling the direct study of grafting reactions, reliably labeling the grafting sites (surface silanols) would enable the more widespread use of ^{17}O NMR to characterize the structure of supported catalysts,²⁰ including their three-dimensional structure.²³

Direct hydroxyl exchange readily occurs with tertiary alcohols at lower pH values.³⁶ The process is known to undergo an $\text{S}_{\text{N}}1$ -type mechanism, which can possibly be extended to the surface silanols on silica supports (Figure 1b). Although hydroxyl enrichment via an $\text{S}_{\text{N}}2$ mechanism is also known,³⁷ this mechanism is likely sterically forbidden on silica surfaces (Figure 1c). Both nucleophilic substitution mechanisms are expected to be strongly pH-dependent, which could provide a means to increase the exchange rate.

To study the rate of hydroxyl exchange, if any, we performed room temperature *in situ* ^{17}O magic-angle spinning (MAS) NMR experiments using a uniformly-enriched Si^{17}O_2 material and natural abundance water. The exchange of ^{17}O -enriched silanols with water should lead to an apparent growth in the ^{17}O NMR signal intensity for liquid $^{17}\text{OH}_2$ given ^{17}O 's natural isotopic abundance of 380 ppm. Additionally, the growth of this signal can be used to measure the rate of oxygen exchange along with its pH-dependence.

Figure 2a shows the evolution of the ^{17}O NMR spectrum of Si^{17}O_2 that was wetted with natural abundance water over a period of approximately 90 minutes. Two signals can be discerned, namely a sharp resonance at 0 ppm from liquid $^{17}\text{OH}_2$, and a broader shoulder resonance to a higher frequency from the siloxanes of the Si^{17}O_2 .³³ There is a strong growth in the $^{17}\text{OH}_2$ signal, indicating rapid oxygen isotope exchange with

the silica surface. We saw no discernible change in the intensity of the siloxane signal. Assuming first-order kinetics, we measured a rate of oxygen exchange of 3.37 h^{-1} . We repeated the experiment in acidic and basic conditions (Figure 2b,c, Table S1). The pH-dependence of the exchange rate was found to be negligible. Given that $\text{S}_{\text{N}}1$ -type hydroxyl exchange is expected to occur at a rate that is proportional to the hydronium ion concentration,³⁶ which would have spanned six orders of magnitude in our experiments, we can conclude that the reaction does not proceed through a mechanism that is of first order in the concentration of hydronium ion (an $\text{S}_{\text{N}}1$ -type mechanism).

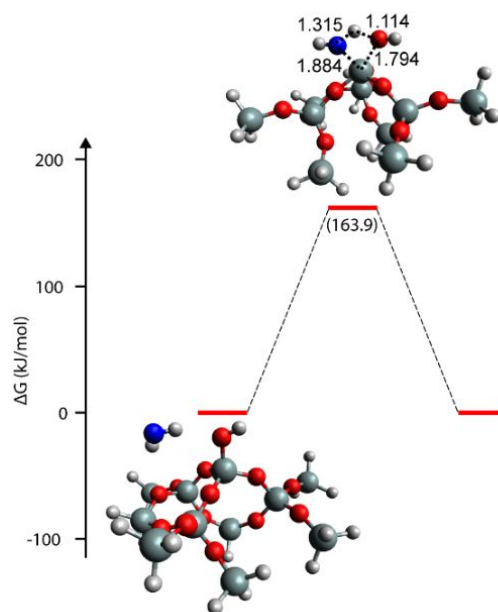


Figure 3. DFT-calculated hydroxyl exchange reaction pathway from Figure 1d. Internuclear distances are in Å. Note that the reactants and products are chemically identical.

Recently, Strohmann and co-workers reported $^{16}\text{O}/^{18}\text{O}$ -exchange at room temperature between silanols in silicon-stereogenic compounds and ^{18}O -enriched water.³⁸ They found that the exchange largely retained the silicon's stereochemistry,

but no mechanistic explanation was reported. This observation counters the racemization and stereocenter inversion that is expected from S_N1 and S_N2 reactions, respectively, again suggesting that silanols undergo oxygen exchange through an orthogonal mechanism. One such possible orthogonal mechanism has been proposed by Liu and co-workers who studied the mechanism for the related alkoxysilane hydrolysis reaction using density functional theory (DFT) calculations.³⁹ They suggested that the reaction proceeds through a 4-centered transition state (**Figure 1d**). This suggested mechanism would be pH-independent and retain configuration in hydroxyl exchange, as we observed experimentally. To this aim, we performed DFT calculations to calculate the room temperature hydroxyl exchange reaction barrier using a silica surface cluster model based on the periodic amorphous silica models of Ugliengo and co-workers.^{40,41} We calculated an activation energy of 163.9 kJ/mol (**Figure 3**), which closely mirrors that calculated by Liu *et al.* for analogous alkoxysilane hydrolysis reactions.³⁹ Experimental reaction rates measured for alkoxysilane hydrolysis are also comparable to those measured here for hydroxyl exchange.⁴² Note that the barrier may be further lowered in transition states that involve a greater number of water molecules.⁴³

The *in situ* ^{17}O MAS NMR experiments further suggest that it may be fairly trivial to prepare silica materials that are selectively-labeled with ^{17}O at either the siloxane or silanol moieties. Specifically, the silica material can be wetted with $^{17}\text{OH}_2$ for an hour and then dried at room temperature to selectively label the silanols. The procedure in **Figure 1a** can also be used to prepare a uniformly- ^{17}O -enriched material which, when exposed to a humid atmosphere, will naturally lose its ^{17}O -labeled silanols by $^{16}\text{O}/^{17}\text{O}$ exchange, thus forming a silica material selectively labeled in only the siloxanes. We prepared these two materials and characterized them using 1D ^{17}O Hahn echo MAS and 2D multiple-quantum (MQ)MAS NMR experiments (see **Figure 4**).

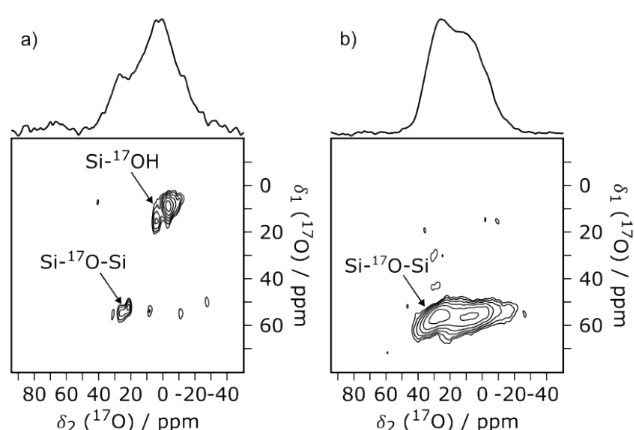


Figure 4. ^{17}O Hahn echo MAS (top) and MQMAS (bottom) spectra acquired for silica that was selectively enriched at the (a) silanol or (b) siloxane positions at 14.1 T.

For the sample labeled at the silanol positions shown in **Figure 4a**, we mainly observe a single resonance at 9 ppm in the

isotropic dimension of the MQMAS spectrum assigned to silanols. A weak siloxane signal is observed at 52 ppm, corresponding to roughly 25% or all ^{17}O , likely due to vicinal siloxane condensation at room temperature. The ^{17}O MAS and MQMAS NMR spectra acquired for the siloxane- ^{17}O -labeled silica gel material are shown in **Figure 4b**. This ^{17}O MQMAS spectrum clearly displays a single resonance assigned to siloxanes at 56 ppm in the isotropic dimension of the MQMAS, with no indication of silanol labeling. These results indicate the two labeling processes to be highly selective.

In summary, we have demonstrated that silanols on the surface of silica can be selectively exchanged at room temperature with water in mere minutes. It was previously assumed that the primary way whereby ^{17}O could be incorporated into silica was via the breaking and forming of Si-O-Si linkages. The observed direct exchange of silanols with water unveiled new reactivity for silica surfaces. The reaction enables the synthesis of selectively- ^{17}O -labeled silica materials that may be of use for the study of the grafting reactions involved in surface organometallic chemistry. This approach is also far more efficient and less costly for the preparation of heterogeneous catalysts for ^{17}O NMR investigation, given that a single exchange reaction with $^{17}\text{OH}_2$ was shown to be sufficient to replace all the surface hydroxyls with ^{17}O .

Isotope enrichment and DFT calculations were carried out by AA, under the guidance of FP. NMR experiments were carried out by AA and MM, under the guidance of FP. Experiments were conceptualized by FP.

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Conflicts of interest

There are no conflicts to declare.

Data availability

Experimental procedures, rate constants, and DFT-optimized structures are provided as supplementary material. Other data can be obtained by contacting the authors.

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