Supplementary information to the paper

Hydroxylation of Metal Supported Sheet-like Silica Films
by
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I. OD-OH exchange with water:

Figure S1 shows an IRA spectrum from a silica film that was initially hydroxylated with H_2O to form OH containing silanols, and then dosed with D_2O at 100 K and heated to 300 K to desorb the molecular water. Using the OH containing film as a reference, we can assign the positive signal at ~3750 cm^{-1} to the disappearance of OH groups, and the negative signal at ~2765cm^{-1} to the formation of OD species via H-D exchange with the D_2O.
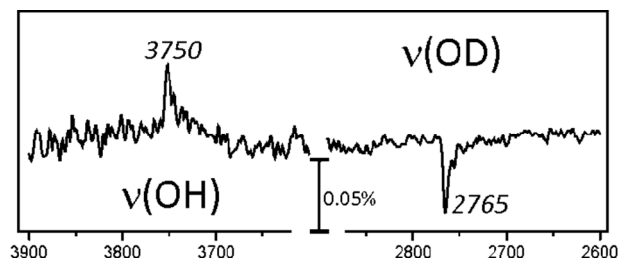

Figure S1. IRA-spectrum of an OH-containing silica film after exposure to D_2O at 100 K and heating to 300 K. The positive ν(OH) signal at 3750 cm^{-1} indicates disappearance of OH species, while formation of OD species is seen as the negative signal at 2765 cm^{-1}.

II. Quantitative analysis of the m/z$^+$ distributions in Fig. 7 of the main text:

In figure S2, we attempt to make use of the m/z$^+$ distribution within the low temperature desorption feature from Fig. 7 to estimate H-D exchange probabilities due to wall reactions within our mass spectrometer, which is presumed to be deuterated due many D_2O experiments conducted within the chamber prior to ammonia adsorption. Provided there is no water contamination, the feature desorbing at ~115 K in figure 7 is presumed to be clean ammonia, which is what we dosed. Based on the desorption temperature, which is ~40 K below that for molecular water, this seems like a fair presumption. In this case, *all* of the signal collected at m/z$^+$ = 19 and 20 must come from collection of NHD_2 and ND_3, respectively. As such, we can assume that the relative intensity of these channels comes *exclusively* from creation of these parent ions. Therefore, we have plotted bars equal to the relative intensities of m/z$^+$ = 19 and 20 that were experimentally collected, and attribute them to ND_2H (dark

grey) and ND_3 (black), respectively. While assignment of these masses was straightforward, the remainder of the channels contains some combination of contributions from the cracking of larger species and transmission of parent ions at those masses.

To account for the cracking contributions, we have used the cracking pattern provided by NIST for NH_3,[1] and make the approximation that all possible configurations of NR_3 will show the same $NR_3 : NR_2 : NR : N = 1 : 0.8 : 0.074 : 0.023$ relative intensities, where R may be any combination of H's and D's, and loss of a D is considered equally as likely as loss of an H. From this, we can conclude that cracking of
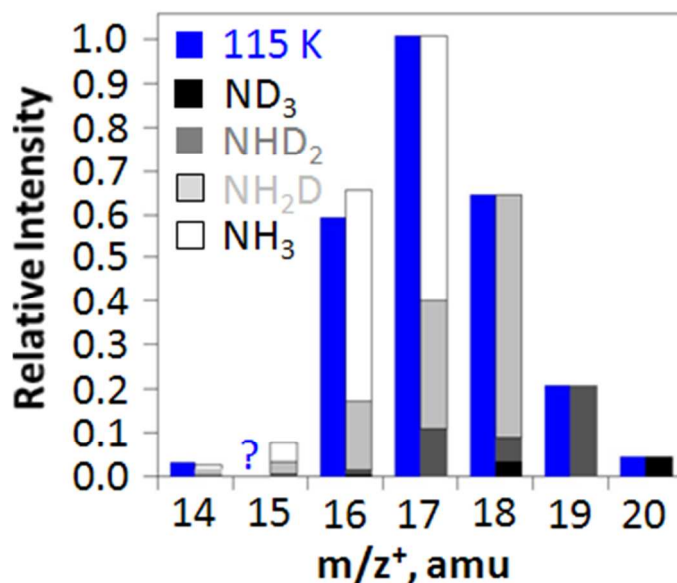

Figure S2. The relative intensities of the various masses detected during desorption of the low temperature feature in figure 7 of the main text are plotted in blue along with a breakdown of the various NR_3 molecules presumed to contribute to the overall intensity of each channel. In this case, R is used to denote either H or D, and cracking contributions have been estimating using NH_3 reference data from NIST.[1]

the ND_3 parent ion will result in contributions to the m/z^+ = 18, 16, and 14 signals, such that 80% of the primary signal will contribute to ND_2^+ (18), 7.4% to ND^+ (16), and 2.3% to N^+ (14). To denote the source of origin, these contributions have been included as black bars at the appropriate masses. For NHD_2, however, we have to consider that loss of an R might mean an H or a D. Since, we have 1H and 2 D's, loss of an H (18) is half as likely as loss of a D (17). By the same token, loss of an H and a D (16) is twice as likely as the loss of 2 D's (15). By this logic, we conclude that cracking of the NHD_2^+ parent ion (dark grey) leads to contributions at m/z^+ = 14, 15, 16, 17, and 18 equivalent to 2.3%, 2.5%, 4.9%, 53.3%, and 26.7% of the primary signal, respectively. After accounting for cracking from ND_3 and NHD_2, the remainder of the m/z^+ = 18 signal must come from the collection of NDH_2 species (light grey). After again applying the cracking procedure to this species, we can finally attribute the unaccounted m/z^+ = 17 signal to collection of NH_3 species (white).

Given the degree to which our cracking contributions approximate the relative intensities of masses 14 and 16, and presumably 15, we can conclude that our NIST-based cracking assumptions are not terribly unreasonable. Furthermore, if we assume that the species leaving the sample in this desorption feature was contaminant-free NH_3 prior to entry into the mass-spectrometer, then we can estimate the likelihood of exchanging 1, 2, or all 3 of the hydrogens for deuterium within the MS. Given the presumed cleanliness of the ammonia dose, and the low desorption temperature of this feature, molecular desorption of unreacted NH_3 would not be unreasonable.

Using the above methodology, with an upper limit of 1 H-D exchange per hydrogen constituent, we predict the likelihood for exchange of 0, 1, 2, and 3 hydrogen groups to be 0.43, 0.39, 0.15, and 0.03, respectively. If we now assume that the substance desorbing in the second feature in Fig. 7 (150 K) is exclusively NDH_2, then we can directly calculate the m/z^+ distribution that would be expected based on exchange within the MS and subsequent cracking. For this, we again treat the H and D constituents equally and assume that the D-substitution probabilities determined for NH_3 remain constant for NR_3, where R is again any combination of H's and D's.

If we start by first considering mass 20, which must still reflect ND_3 species, we now have two possible routes of formation. All three of the R's can be replaced (black), or the two H's can be selectively exchanged (dark grey), which will be half as likely as exchange of an H and a D to form NHD_2 (19). By the same logic, exchange of 1 R group (light grey) will be twice as likely to form NHD_2 (19) as NDH_2 (18). If we complete the plot by including the fractional abundance of NDH_2 expected to survive without exchanging (white) and all cracking contributions (diagonal lines), then we note a distribution of fractional abundances that closely resembles the distribution observed for the 150 K desorption feature in Figure 7. Based on the quality of this fit, we conclude that the majority of the molecules desorbing at 150 K are in fact NDH_2, which have undergone 1 H-D exchange with OD silanol groups at the silica interface.

Figure S3. The fractional intensities of the various masses detected during desorption of the high temperature feature in figure 7 of the main text are plotted in red along with a distribution predicted using the procedures described in the text for the desorption of pure NDH_2.

Reference:

1. NIST Standard Reference Database Number 69, ©2011
http://webbook.nist.gov/cgi/cbook.cgi?ID=C7664417&Units=SI&Mask=200#Mass-Spec.