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Are the Brønsted acid sites in amorphous silica-alumina bridging?

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Competing models exist to explain the differences in the activity of zeolites and amorphous silica-aluminas. Some postulate that silica-alumina contains dilute zeolitic bridging acid sites, while others favor a pseudo-bridging silanol model. We employed a selective isotope labeling strategy to assess the existence of Si-O(H)-Al bonds using NMR-based distance measurements.

Aluminosilicate catalysts are among the most widely used heterogeneous catalysts in the petrochemical industry.[1,2] These include zeolites in addition to amorphous silica-alumina (ASA) that are used for their Brønsted acidity. The allure of ASA catalysts is primarily driven by the restrictive micropore sizes of crystalline zeolites, which limit their application for the conversion of larger molecules. Although it is generally assumed that ASA catalysts contain analogous sites to those found in zeolites, their activity towards hydrocarbon cracking is orders of magnitude lower than that observed in zeolites,[3] which has led to competing models for acid sites in ASA.

In 1998, Trombetta *et al* proposed that the amorphous nature of ASA could lead to the formation of acid sites wherein a Lewis acidic Al center in proximity to a silanol can stabilize the latter's conjugate base and thus increase Brønsted acidity.[4] This model was further developed by Chizallet and Raybaud using molecular modeling methods, with the sites being termed pseudo-bridging silanols (PBS, **Figure 1b**).[5-9] PBS are structurally distinct from the bridging Brønsted acid sites (BAS, **Figure 1c**) found in zeolites. There, the substitution of a lattice Si center by Al creates a negative charge that is compensated by a highly acidic proton. Lattice forces in zeolites prevent the dissociation of the silanol from Al and as such, PBS sites are expected to be comparatively weaker acids than zeolitic BAS.

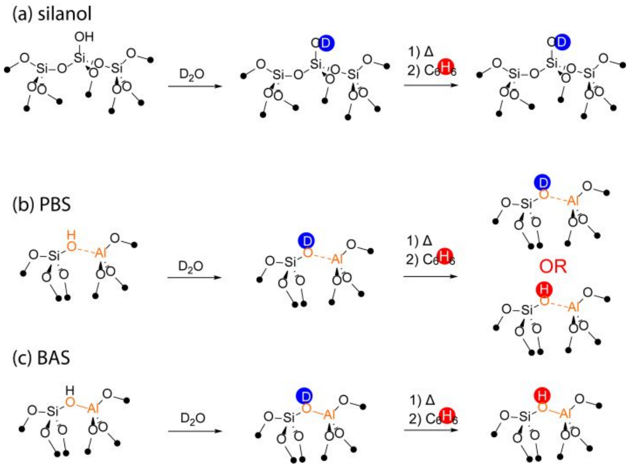

Figure 1. Structures of silanol (a), PBS (b) and BAS (c) sites and their expected behavior following sequential H/D exchange with D_2O and benzene.

Experimental evidence for the existence of PBS have been obtained using an array of nuclear magnetic resonance (NMR) experiments. These include the measurement of ^1H-^{27}Al and ^{17}O-^{27}Al distances to probe for the existence of a HO-Al bond,[10-12] in addition to ammonia titration experiments that have demonstrated that certain silanols are able to protonate ammonia.[13] While few argue against the existence of a high concentration of PBS sites in ASA, some have questioned their relevance in catalysis.[14] The competing argument is that ASA contains a low number of BAS responsible for the bulk of the catalytic activity. Infrared (IR) spectroscopy experiments performed using probe molecules, such as CO and pyridine, have provided evidence for the existence of distinct populations of acid sites, presumably BAS and PBS, with catalytic activity in alkane hydroconversion and benzene H/D exchange being correlated with the population of the more dilute acid site.[14-18] The assignment of the dilute species to BAS has, however, come under scrutiny;[19] the OH stretching frequency is non-trivially correlated to longer-range structure; such as the existence of a HO-Al bond.[19,20] Conclusively proving the existence of BAS in ASA would require evidence of a HO-Al bond. Recent NMR work has provided chemical shift evidence

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Electronic Supplementary Information (ESI) available: Experimental descriptions, ^{17}O DNP data, and ^1H NMR data on ZSM-5. See DOI: 10.1039/x0xx00000x for the existence of such a species[21] through the detection of a hydroxyl ^1H at 4.6 ppm that is correlated with a ^{27}Al site with a large C_Q. Hydroxyl chemical shifts are, however, notoriously difficult to analyze,[22] as are ^{27}Al quadrupolar coupling constants,[23] and as such the importance of BAS in ASA materials remains an open question.

^{17}O-^{27}Al distance measurements have been used to probe such structures in the past,[12] but the methods did not provide a means of distinguishing catalytically active and inactive hydroxyls. As such, while no evidence of a Si-O(H)-Al moiety was obtained, the experiments also failed to detect the aforementioned dilute catalytic species. Herein, we seek to conclusively identify the structure of the active site detected in these earlier IR studies using a combination of site-specific isotope labeling and NMR-based distance measurements.

Among the methods used to study acid sites in zeolites is the Brønsted site-catalyzed H/D exchange of benzene, or other hydrocarbons.[24] This reaction has been used to study the activity of BAS in various zeolites *in situ* using ^1H NMR[25-27] as well as to probe the concentration of active sites in ASA by IR spectroscopy. In the former experiment, perdeuterated benzene (C_6D_6) is used as the reactant and ^1H NMR is used to probe the production of protonated benzene. We began by replicating the aforementioned experiment, by reacting 40 µL of C_6D_6 (3.5 mmol deuterons) with activated ZSM-5 and ASA catalysts (39.6 and 44.5 mg, respectively) in a magic angle spinning (MAS) rotor. These conditions ensure an excess of deuterons given that the highest BAS density of 1 site per Al in ZSM-5 would yield a maximum BAS count of 0.026 mmol. Reactions were carried out at 22 °C and a ^1H MAS (ν_R = 5 kHz) NMR spectrum was acquired every 60 s. At these low MAS frequencies, it was not possible to follow the change in the hydroxyl densities directly, but we saw a noticeable growth in the benzene ^1H signal for both catalysts, which enabled their rough quantitation; this is plotted in **Figure 2** below.

We observed an H/D exchange rate of 3.7 s^{-1} in the case of the ASA, while the exchange was slower, and biexponential, for the ZSM-5 with rates of 1.0 and 0.1 s^{-1}. We note, however, that estimating the exchange rate for the ASA is challenging, due to the lower changes in signal intensity, and it was found to be highly dependent on external factors, such as water content.[28,29] The greatest difference between the materials was the site density, with the active sites having a concentration of 3.7 ± 1.0 µmol/g and 160 ± 30 µmol/g in the case of the ASA and ZSM-5, respectively. The faster-exchanging component of the zeolite had an estimated concentration of 35 ± 10 µmol/g. These concentrations are largely in line with those reported from previous IR spectroscopy experiments,[18] but are likely underestimated due to exchange with moisture in the glovebox, which we found to be significant. The relative difference between the two materials, however, is expected to be reliable. While it may be tempting to equate the slower exchange rate to BAS-silanol exchange,[30] BAS have roughly twice the concentration of the silanols in this material (**Figure 3a (i)**), suggesting that the difference may instead originate from a plurality of sites or limitations in mass transport. Multisite behavior has indeed been reported for ZSM-5.[31-33]

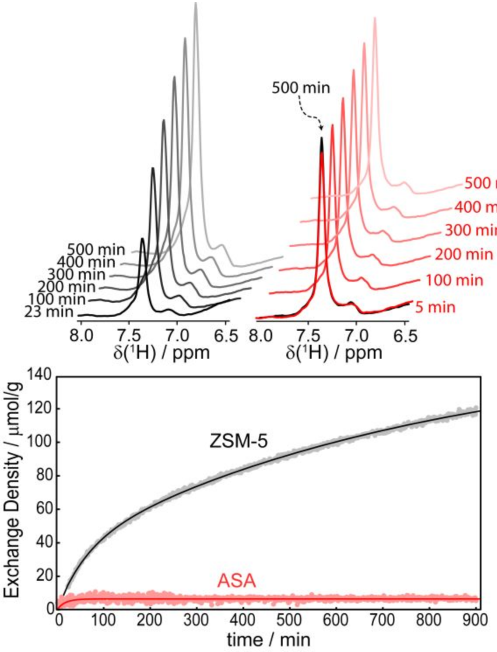

Figure 2. Comparison of the growth in the intensity of the benzene ^1H NMR signal as a function of the reaction time with the ZSM-5 (grey) and ASA (red) catalysts. NMR spectra extracted after a given reaction time are shown on the top while the normalized integrated intensities are plotted below. The spectrum taken after 500 minutes of reaction with the ASA catalyst is overlayed as a grey dashed spectrum over the initial spectrum to show the weak intensity growth. Intensities were normalized to have the extrapolated benzene ^1H NMR signal intensity at time zero equal the residual ^1H concentration of the solvent (0.5 %). Data are fitted to the following expressions, ZSM-5: 156.3 µmol/g $(1 - 0.78\exp(-0.1\ s^{-1}t) - 0.22\exp(-1.0\ s^{-1}t))$; ASA: 3.7 µmol/g $(1 - \exp(-3.7\ s^{-1}t))$.

We will briefly mention that higher catalytic activity toward H/D exchange has been observed in ASA catalysts with higher aluminum concentrations.[34] In these materials, a distinct active site has been postulated to exist, corresponding to a μ_3-OH coordinated to two aluminum centers and one silicon.[35,36] Proximate aluminum sites coordinated to chemisorbed water may also help reprotonate BAS. Due to silica-alumina materials' adherence to Loewenstein's rule,[37,38,12] these sites are not expected to be present in large numbers on our ASA, which possesses a 30% Al concentration.

Knowing that *in situ* NMR experiments can replicate the IR spectroscopy results,[18] we selectively labeled the Brønsted sites that are active towards benzene H/D exchange *ex situ*. Briefly, in one sample, all hydroxyls were first enriched with deuterium using D_2O. Then, the catalysts were activated at 450 °C under dynamic vacuum for a period of 16 hours. The obtained activated and deuterated catalysts were then reacted with dry benzene in a glovebox for 15 to 60 minutes to selectively install ^1H spins on the active sites (**Figure 1**) and dried under dynamic vacuum for ~6 hours. We performed analogous experiments using the as-prepared catalysts and perdeuterated, dry, benzene.

The ^{1}H MAS NMR spectrum of ZSM-5 is shown in **Figure 3a (i)** where we can clearly distinguish resonances from BAS in ZSM-5 at 2.0 and 4.2 ppm. In contrast, for the ASA (**Figure 3a (ii)**) we can only detect a silanol resonance and a continuum of progressively more deshielded hydroxyls.[10] The ^{1}H{^{27}Al} symmetry-based rotational-echo saturation-pulse double-resonance (S-RESPDOR) experiment,[39-41] however, reveals a distinct population of sites with chemical shifts ranging from 2 to 10 ppm that features stronger ^{1}H-^{27}Al interactions. When this ASA is exposed to C_6D_6, we see a depletion in intensity where this signal appears, suggesting that the site is catalytically important (**Figure 3a (ii) blue**). If we instead deuterate the support with D_2O prior to an exchange with C_6H_6 we see a large decrease in signal intensity with the residual intensity coming either from exchange with moisture in the glovebox or inaccessible hydroxyls (**Figure 3a (iii)**). This is also reproduced by IR spectroscopy (**Figure S2**). After exposure to C_6H_6 we see the appearance of the signal from what is, clearly, the catalytically important acid site. We believe this to be the first resolution of the ^{1}H NMR signal from a the Brønsted sites in ASA using 1D NMR.

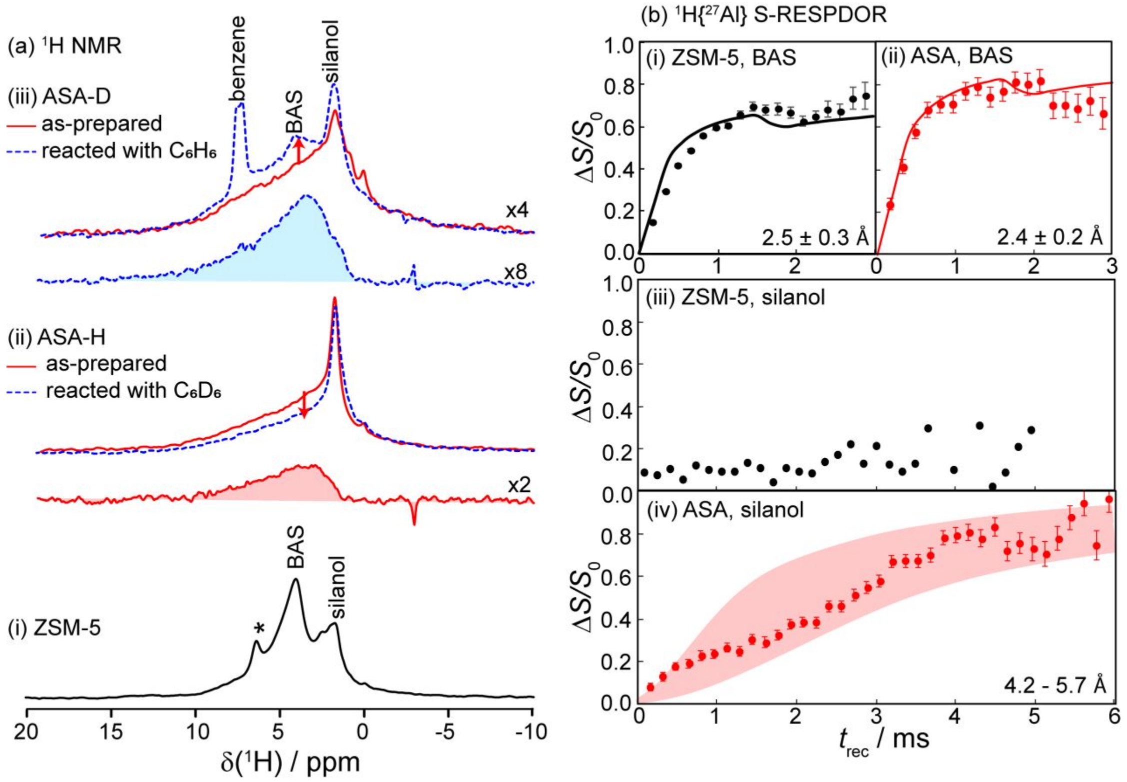

Figure 3. (a) ^{1}H MAS NMR spectra acquired on thermally activated ZSM-5 (i), protonated (ii) and deuterated (iii) ASA. In (ii) and (iii) spectra of the as-prepared materials are shown in red while those following benzene H/D exchange are shown in dashed blue lines. Shaded spectra correspond to ^{1}H{^{27}Al} S-RESPDOR difference spectra acquired with 960 µs of $SR4_1^2$ dipolar recoupling. (b) ^{1}H{^{27}Al} S-RESPDOR dephasing curves acquired for the Brønsted and silanol sites in both catalysts, as indicated on the Figure. In (a,i) an asterisk denotes a minor resonance from benzene that was captured from the atmosphere of the glovebox.

To identify the active site in ASA, we acquired ^{1}H{^{27}Al} S-RESPDOR data to measure a quantitative H-Al distance; an approach often used to study BAS in zeolites.[42-45] This distance is expected to measure 2.5 Å for a BAS and 3.0-4.4 Å for PBS. For the ZSM-5 catalyst, we observed negligible dephasing for the silanol defects, and a H-Al distance of 2.5 ± 0.3 Å for the BAS (**Figures 3b (i) and (iii)**). Residual benzene was also found to be tightly associated with the BAS, which may explain why it is not eliminated by dynamic vacuum (**Figure S4**).

In the case of the active site in the labeled ASA material, we measured a H-Al distance of 2.4 ± 0.2 Å, confirming that this site is of the bridging variety and structurally analogous to the Brønsted sites found in zeolites (see **Figure 3b (ii)**). No evidence was found for the formation of active μ_3-OH sites,[35] which would have a doubled dipolar dephasing rate.

Non-negligible dephasing was observed for the silanol species in this case (**Figure 3b (iv)**) due to the higher Al loading of 30 % (versus 4% for the zeolite). Through χ^2 analysis[46] we found this dephasing level to cover H-Al distances ranging from 4.2 to 5.7 Å. In number, these sites outweigh the BAS (**Figure 3a (ii)**), which would explain the rather long ^{17}O-^{27}Al distances that were measured in a previous study.[12] We attempted to measure the ^{17}O-^{27}Al distance in the BAS-labeled ASA material, but the material degraded under dynamic nuclear polarization (DNP) conditions[47] (see **Figure S5**).[48,49]

To summarize, we applied active-site labeling strategies to probe the Brønsted sites in amorphous silica-alumina. Our results confirmed that the materials' activity is dominated by the presence of a few highly active bridging acid sites, analogous to those found in zeolites. Specifically, benzene H/D exchange experiments selectively labeled sites possessing a ^{1}H-^{27}Al distance of 2.4 ± 0.2 Å; far too short to suggest the relevance of pseudo-bridging sites in C-H activation. This experiment does not, however, rule out the importance of PBS sites in other reactions, such as alcohol dehydration reactions.[9]

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Author Contributions

Silica alumina materials were synthesized by P.C., NMR experiments were performed by W.S. and T.Y.Z., and experiments were conceptualized by F.A.P.

Conflicts of interest

There are no conflicts to declare.

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