Brønsted acid sites based on penta-coordinated aluminum species

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Zeolites and amorphous silica-alumina (ASA), which both provide Brønsted acid sites (BASs), are the most extensively used solid acid catalysts in the chemical industry. It is widely believed that BASs consist only of tetra-coordinated aluminum sites (AlIV) with bridging OH groups in zeolites or nearby silanols on ASA surfaces. Here we report the direct observation in ASA of a new type of BAS based on penta-coordinated aluminum species (AlV) by ²⁷Al-{¹H} dipolar-mediated correlation two-dimensional NMR experiments at high magnetic field under magic-angle spinning. Both BAS-AlIV and -AlV show a similar acidity to protonate probe molecular ammonia. The quantitative evaluation of ¹H and ²⁷Al sites demonstrates that BAS-AlV co-exists with BAS-AlIV rather than replaces it, which opens new avenues for strongly enhancing the acidity of these popular solid acids.

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The need for efficient and environmentally benign chemical processes has forced the replacement of harmful and corrosive liquid acids by solid acids in various fields of catalysis, including fine chemistry\(^1\)–\(^3\), renewable energy production\(^4\)–\(^6\), oil refining and petrochemical industries\(^7\)–\(^9\). Silicon- and aluminum-based mixed oxides provide moderate and strong Brønsted acidity and are among the most popular solid acids used in current chemical processes\(^10\)–\(^12\). Briefly, the solid acid catalysts can protonate hydrocarbon molecules to form carbocations and drive important reactions, such as cracking, hydrocracking, isomerization, alkylation and aromatization\(^10\)–\(^13\), through surface complexes or transition states\(^15\).

Crystalline zeolites and amorphous silica-alumina (ASA) are two main types of solid acids that contain Brønsted acid sites (BASs). It has been widely believed that only tetra-coordinated aluminum (Al\(^{IV}\)) atoms are able to contribute to the formation of BASs in nature\(^16\). In crystalline zeolites, the BASs are formed by protons, which compensate the negatively charged oxygens induced by the substitution of Si atoms by Al\(^{IV}\) in the framework. The structure of these sites is well known as the bridging Si(OH)Al\(^{IV}\) model (Fig. 1a)\(^15\)–\(^17\). Replacing Si atoms by more Al\(^{IV}\) species can enhance the density of BASs, but it reduces the mean electronegativity of the framework, which thus leads to a decrease of the overall acid strength of BASs\(^18\),\(^19\). Similarly, Al\(^{IV}\) species incorporated into the amorphous silica network are able to generate BASs on ASA\(^9\),\(^20\),\(^21\). The proximity between Al\(^{IV}\) and silanol sites in ASA has recently been observed by nuclear magnetic resonance (NMR) correlation experiments between \(^29\)Si and \(^27\)Al nuclei, the sensitivity of which was enhanced by dynamic nuclear polarization\(^22\). However, the strength of these BASs is generally lower than that on crystalline zeolites\(^7\) and thus the presence of bridging OH groups (Fig. 1a) in ASA is still strongly under debate\(^22\),\(^23\).

A flexible coordination between the Al\(^{IV}\) atom and the neighbouring silanol oxygen atom (Fig. 1b)\(^21\),\(^24\)–\(^25\) or a pseudo-bridging silanol (PBS) with a nearby Al atom (Fig. 1c)\(^26\),\(^27\) have been proposed\(^22\), to account for the longer Al-O distances (2.94–4.43 Å) in ASA\(^26\), with respect to those in the crystalline zeolite framework (1.88–2.0 Å)\(^28\). So far, most efforts focus on tuning the concentration of Al\(^{IV}\) as the main route to increase the Bronsted acidity on zeolites or silica-alumina\(^29\)–\(^33\). However, Al\(^{IV}\) species tend to condense, to form an alumina phase at high Al/Si ratios\(^34\)–\(^36\), leading to the decrease of Bronsted acidity. For ASA containing solely BASs based on Al\(^{IV}\) species (BAS-Al\(^{IV}\)), the maximum Bronsted acidity has been obtained at 30 wt% Al loading\(^37\),\(^38\). In spite of the different BAS models, only Al\(^{IV}\) species have been experimentally confirmed to contribute to the formation of BASs in these catalysts. Al\(^{IV}\) and Al\(^{VI}\) species have been shown to act as Lewis acid sites on ASA and zeolites, but, to the best of our knowledge, no experimental evidence of BASs involving these sites has been reported so far\(^39\)–\(^42\).

Herein, we provide the direct experimental evidence for a new type of BAS-Al\(^{IV}\) in ASA by dipolar-mediated heteronuclear multiple quantum correlation (D-HMQC) two-dimensional (2D) NMR experiments, which allow the detection of protons via \(^27\)Al nuclei, hereafter noted \(^{27}\)Al-[\(^1\)H], hence probing the spatial proximities between different Al species and surface protons\(^43\)–\(^45\). These experiments show that ASA can contain a large amount of Al\(^{IV}\) species located near SiOH groups. The acidity of these surface BAS-Al\(^{IV}\) sites has been demonstrated in this research by the adsorption of basic ammonia molecules, which react with BAS-Al\(^{IV}\) to form surface ammonium ions.

Results

Probing the connectivity between Al\(^{IV}\) species and SiOH groups.

The ASA used in this work (see Supplementary Methods) have been prepared according to a previously described procedure\(^9\), which generates ASA nanoparticles with a large amount of Al\(^{IV}\) species. The ASA powders are designated as SA/X, where X is 10 or 50, indicating the molar fraction of Al in the precursor with respect to the total amount of Al and Si atoms. The obtained ASAs have tunable BAS acidity strengths ranging from moderate (SA/10 has an acidity close to zeolite H-X) to large (SA/30–70 have stronger BASs than zeolites H-Y and ZSM-5), depending on the aluminum content, as confirmed by both \(^{13}\)C magic angle spinning (MAS) NMR investigation with probe molecule acetone and ammonia-temperature program desorption (TPD)\(^9\). The ASAs exhibited excellent catalytic performances for the conversion of phenylglyoxal with various alcohols, better than that of dealuminated zeolite Y, which hitherto was considered to be the most active solid acid in phenylglyoxal conversion\(^7\).

The formation of BAS requires the aluminum atoms to be close to SiOH groups. Such proximity induces a dipolar coupling between \(^2\)Al and \(^1\)H nuclei, which can efficiently be probed by D-HMQC NMR 2D experiments based on coherence transfers via the \(^1\)H–\(^{27}\)Al dipolar couplings\(^46\),\(^47\). As shown in Fig. 2, the correlation at \(\delta_{27A} = 50\) p.p.m. and \(\delta_{1H} = 1.9\) p.p.m. in the \(^{27}\)Al-[\(^1\)H] D-HMQC 2D spectrum of dehydrated SA/50 indicates a close proximity between Al\(^{IV}\) species and the proton of SiOH groups. This correlation is ascribed to the Si-OH···Al\(^{IV}\) coordination: the typical BAS-Al\(^{IV}\) often described for ASA (Fig. 1c)\(^16\). A weak very correlation at \(\delta_{27A L} = 10\) p.p.m. and \(\delta_{1H L} = 1.1\) p.p.m. is assigned to the non-acidic terminal Al\(^{VI}\)OH groups often observed on the surface of silica-alumina or zeolites, whereas the low-field broad hump at ca. 6 p.p.m. in the
AlIV-based BASs. In zeolites, the substitution of a framework Si atom by an AlIV one to form one SiOHAI acid site (Fig. 1a) can shift the 1H NMR signal of SiOH from ca. 1.8 to 3.6–5.2 p.p.m. (ref. 16). For these catalysts, BAS could be directly evidenced by the cross-peak in 27Al-{1H} D-HMQC 2D spectrum between AlIV species (δ27Al = 60 p.p.m.) and the bridging OH groups (δ1H = 4.3 p.p.m.)5,6. However, previous works have shown that the Al atoms with neighbouring SiOH groups (Fig. 1b,c) do not produce such a shift of the 1H MAS signal of these groups5,6,9,16,20,21. Supplementary Fig. 1a,b show that the 1H signal of SA/10 and SA/50 is centered around 1.9 p.p.m., thus indicating a majority of flexible or PBS coordination rather than zeolitic bridging coordination between SiOH groups and either AlIV or AlV species.

Experiments using probe molecules have confirmed the role of flexible or PBS Si-OH...AlIV coordination as BAS in ASA3,6,9,16,20,21. Similar methods using ammonia probe molecules were applied here to demonstrate the acidity of the Si-OH...AlIV coordination observed in dehydrated SA/10 and SA/50 (ref. 16). For these samples loaded with ammonia, the 1H signal of ammonium ions was observed at δ1H = 6.7 p.p.m., as shown in Supplementary Fig. 1c,d, and commented in Supplementary Note 1. The formation of these ions shows that ammonia reacts with BAS of SA/10 and SA/50.

27Al-{1H} D-HMQC experiments were also carried out to determine the nature of BAS, which protonate the ammonia molecules. Such a strategy based on 1H,27Al correlations has been applied for [Al]MCM-41 loaded with ammonia. For such catalysts, ammonium ions (δ1H = 6.7 p.p.m.) were only coupled to AlIV species (δ27Al = 56 p.p.m.)44. Hence, there was only evidence for BAS-AlIV on the surface of [Al]MCM-41, which protonated ammonia to ammonium ions. As seen in Fig. 3, a correlation between NH4+ ions (δ1H = 6.7 p.p.m.) and AlIV (δ27Al = 50 p.p.m.) is also observed in 27Al-{1H} D-HMQC spectra of SA/10 and SA/50, showing that the BAS-AlIV sites are also present on the surface of ASAs (Fig. 4a). Interestingly, these spectra also exhibit cross-peaks between AlV species (δ27Al = 30 p.p.m.) and NH4+ ions (δ1H = 6.7 p.p.m.) in both SA/10 and SA/50. As seen in Fig. 3e, the intensity of this AlIV-NH4+ cross-peak is comparable to that of the AlIV-NH4+ one. Given the BAS density ranging from 0.16 to 0.36 H+ nm−2 in the investigated ASA samples (Supplementary Table 1), each ammonia molecule only interacts with one BAS. The distance between the aluminum atom and the neighbouring silanol oxygen in ASA ranges from ca. 2.94 to 4.43 Å26 and the N–H bond length in ammonia is only 1.02 Å48. As the heteronuclear coherence transfer in 27Al-{1H} D-HMQC is only effective up to a few angstroms, the protons of Si–O− (NH4)+...Al environment only interact with the neighbouring Al. The observation of an AlV-NH4+ cross-peak in Fig. 3 at (30, 6.7) p.p.m. directly confirmed that ammonia is protonated on a BAS containing AlV: the Si-OH...AlV group.

The comparison of Supplementary Fig. 1c,d shows that more ammonia molecules are protonated on BAS-AlIV in SA/50 than in SA/10. Combined with quantitative 1H NMR investigations (Supplementary Fig. 1) and the quadrupolar parameters (Supplementary Table 2 and Supplementary Note 2) obtained from 27Al one-dimensional MAS (Supplementary Fig. 3) and 2D multiple quantum MAS (Supplementary Fig. 2) NMR experiments, the analysis of 27Al cross-peak intensities in 27Al-{1H} D-HMQC spectra (Supplementary Fig. 4 and Supplementary Note 3) revealed that the population densities of both BAS-AlIV and -AlV on SA/50 (0.078 and 0.053 mmol g−1) were both higher than those of SA/10 (0.058 and 0.039 mmol g−1). This result suggests that BAS-AlIV and -AlV can co-exist on the surface rather than replacing each other and the population of both acid sites can be amplified by increasing Al content. Thus, this observation is promising for enhancing the population of BAS on ASA without limitation imposed by the Al.
AlIV and AlV species can co-exist on the surface of ASA. This very important implication emerging from this work is that both and show comparable acidity to protonate ammonia. Finally, a creating high-performance solid acid catalysts containing

By analogy, similar structures between SiOH and Al atom (Fig. 1c) have been proposed for the flexible coordination of SiOH and Al (Fig. 1b), or a pseudo-bridge Lewis sites (Supplementary Note 5).

As shown in Fig. 1, a surface bridging SiOH-AlI (Fig. 1a), a flexible coordination of SiOH and Al (Fig. 1b), or a pseudo-bridge between SiOH and Al atom (Fig. 1c) have been proposed for the formation of BAS-AlIV on ASAs. By analogy, similar structures might also contribute to the formation of BAS-AlV. The PBS model permits an explanation of the observation of the 27Al NMR signal of SiOH at 1.9 p.p.m. in both Fig. 2 and Supplementary Fig. 1, whereas this 1H signal of bridging OH groups (Fig. 1a) should occur at 3.6–5.2 p.p.m. If bridging OH groups are present in the investigated ASAs, their concentration must be below the limit of detection of the one-dimensional NMR MAS spectra of Supplementary Fig. 1. Nevertheless, the current NMR data cannot rule out, in addition to PBS, the presence of bridging silanol groups in low concentration in ASA samples. These elusive strong BASs may also contribute to the catalytic activity in spite of their low concentration. The identification of all catalytic BASs in ASAs is beyond the scope of the present study, which is mainly to report the existence of BASs based on AlIV environments. A final assessment of the local structure of BAS-AlIV will require further experimental and theoretical work.

In summary, a new type of BAS-AlIV has been directly observed by 27Al-{1H} D-HMQC NMR spectroscopy. Hitherto, it was widely accepted that AlIV sites only provide Lewis acidity39–42, and that solely AlIV ones contribute to the formation of BASs in aluminosilicate. However, we prove here by NMR experiments that similar to AlIV sites, AlV ones interact with neighbouring SiOH groups in ASA and behave as BASs in agreement with the PBS model. BAS-AlIV and -AlV seem to be structurally similar and show comparable acidity to protonate ammonia. Finally, a very important implication emerging from this work is that both AlIV and AlV species can co-exist on the surface of ASA. This feature facilitates that the total population density of BAS can be increased up to 70% by increasing the Al content, an amount much higher than the maximum Al loading of ca. 30% at which maximum acidity on ASA containing exclusively BAS-AlIV is achieved37,38. Hence, our findings not only report the existence of a new type of BAS in nature, but also open new avenues for creating high-performance solid acid catalysts containing AlV species, which will be promising for sustainable oil-refining and many industrial chemical processes.

Methods

27Al-{1H} D-HMQC 2D experiment. All NMR experiments were recorded on a Bruker Avance III 18.8 T (1H Larmor frequency of 800 MHz) spectrometer equipped with a 3.2 mm double-resonance MAS probe, in which rotors were spun at ωr = 20 kHz. In the D-HMQC sequence, we have detected the 27Al nuclei to benefit from their fast longitudinal relaxation times and the 27Al dipolar couplings were reintroduced by applying a 1H recoupling on the 1H channel49. The 1H radiofrequency amplitudes for the 90° pulses and the 1H 45° recoupling were equal to 2.5 and 40 kHz, respectively. The central transition selective pulse lengths on 27Al were 8 and 16 μs for 90° and 180° pulses, respectively, that is, radiofrequency field amplitude 1/νr = 10 kHz. The total dipolar recoupling time, τrec, ranged from 700 to 1,000 μs depending on the sample. The 2D spectra resulted from the accumulation of 512 transients for each of 20 τ rec increments with Δτ = 50 μs and a recycle delay = 1 s, that is, a total experiment time of about 3 h. Additional details about NMR experiments are given in the Supplementary Methods.

Data availability. The data that support the findings of this study are available upon request from the corresponding author J.H. and J.-P.A.

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