

Research Highlight

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A focus on the observation of bridging SiOHAl Brønsted acid sites in amorphous silica-alumina

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Aluminosilicate catalysts, including zeolites and amorphous silica-alumina (ASA), are popular solid-acid catalysts, which are widely employed in petroleum refining, biomass conversion and organic synthesis^[1,2]. In particular, ASA is advantageous for the conversion of large molecules, notably those derived from biomass, which are often complex and viscous, and hence, diffuse slowly into the micropores of zeolites. ASA can be prepared by different approaches, including sol-gel synthesis^[3], coprecipitation^[4], flame-spray pyrolysis^[5,6] and atomic-layer deposition^[7] but they exhibit milder Brønsted acidity than zeolites.

Despite extensive studies, the structure of Brønsted acid sites (BAS) in ASA is still highly debated. It has been proposed, notably on the basis of molecular modeling studies, that ASA contains BAS, called pseudo-bridging silanols (PBS), consisting of a silanol in close proximity to an aluminum atom, which stabilizes the silanolate anion and, hence, increases the Brønsted acidity of the PBS^[8-10]. In contrast with bridging Si-O(H)-Al BAS found in zeolites, there is a lack of covalent bonds between O and Al atoms in PBS. Solid-state nuclear magnetic resonance (NMR) experiments, which allowed to probe proximities between ¹H and ²⁷Al nuclei and to measure ¹H-¹⁷O distances in ASA, provided experimental evidence for the existence of PBS in these catalysts and their ability to protonate ammonia^[11-13].



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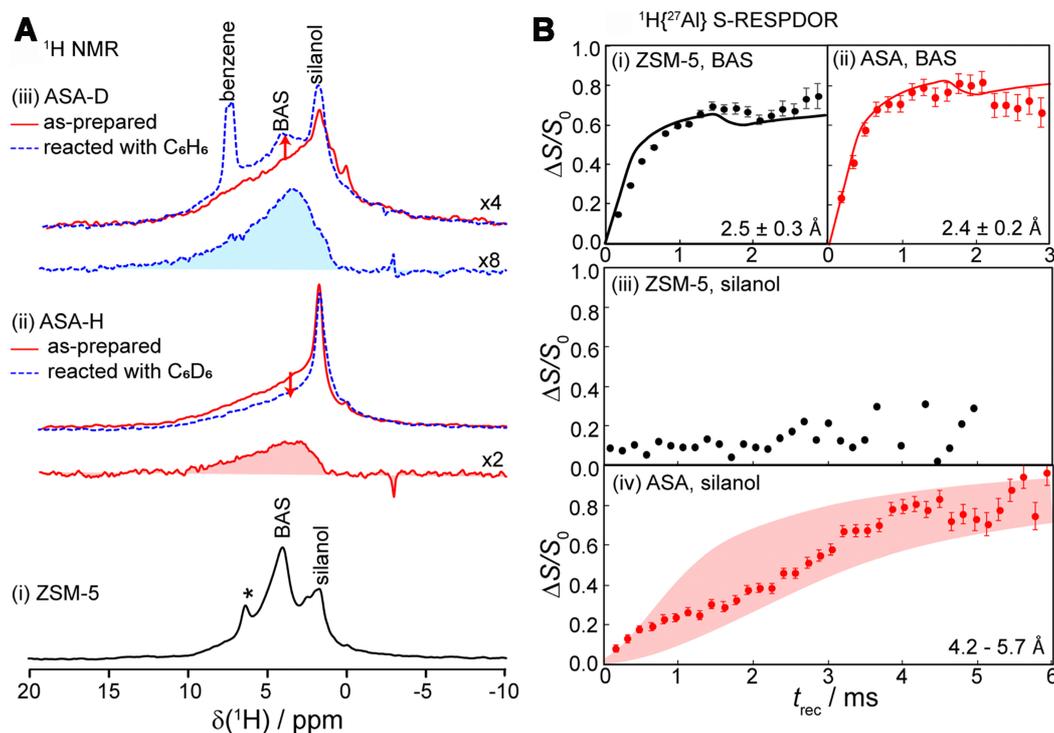


Figure 1. (A) ^1H NMR spectra under magic-angle spinning of (i) thermally activated ZSM-5, (ii) protonated and (iii) deuterated ASA: as-prepared catalyst (red line) and after H/D exchange with benzene (dashed blue line). The shaded spectra correspond to the NMR spectra of protons close to Al atoms, i.e., BAS. It was obtained as the difference between ^1H NMR spectra recorded with and without the recoupling of ^1H - ^{27}Al dipolar interactions; (B) Solid-state NMR measurement of ^1H - ^{27}Al distances for (i and ii) BAS and (iii and iv) other silanol groups in (i and iii) thermally activated ZSM-5 and (ii and iv) partially deuterated ASA. Reprinted with permission from Ref. [17]. Copyright 2023, Royal Chemical Society. NMR: Nuclear magnetic resonance; ASA: amorphous silica-alumina; BAS: Brønsted acid sites.

Nevertheless, the existence of BAS in ASA was suggested by their catalytic activity for the propane cracking and H/D exchange and the presence of sites with distinct acidities, as detected by infrared spectroscopy using probe molecules^[14,15]. Recently, solid-state NMR experiments were conducted at an ultra-high magnetic field (35.2 T), i.e., a ^1H Larmor frequency of 1.5 GHz, to observe the proximity between ^1H and ^{27}Al nuclei and provided the first direct spectral evidence for the existence of BAS in ASA^[16]. However, even at this ultra-high magnetic field, the ^1H NMR spectra of ASA exhibited limited resolution owing to the amorphous nature of these catalysts and the distribution of proton local environments.

To confirm the presence of BAS in ASA, Salvia *et al.* have compared the one-dimensional (1D) ^1H NMR spectra of thermally activated ZSM-5 and ASA [Figure 1A]^[17]. As seen in Figure 1A(i), the ^1H NMR spectrum of ZSM-5 exhibits two resolved resonances at 4.2 and 2.0 ppm, assigned to BAS and non-acidic silanol groups distant from aluminum atoms^[18]. Conversely, the ^1H NMR spectrum of ASA [Figure 1A(ii)] is dominated by a narrow peak of silanol groups, including PBS but also exhibits a broad signal extending from 2 to 10 ppm. This broad signal must stem from hydroxyl groups with a distribution of local environment, which is consistent with the amorphous nature of ASA. Furthermore, these hydroxyl groups are close to ^{27}Al nuclei. The intensity of this broad signal is also reduced when ASA is exposed to deuterated benzene, suggesting that these protons are exchanged with the deuterons of C_6D_6 . To facilitate the observation of these highly acidic sites in ASA, the authors partially deuterated this catalyst with deuterated water and then exposed it to isotopically unmodified benzene. This strategy allowed them to label selectively with protons the Brønsted sites, which are active towards H/D exchange with benzene [Figure 1A(iii)].

Then, they compared the dephasing of ^1H NMR signals under ^1H - ^{27}Al dipolar interactions in ZSM-5 and ASA [Figure 1B]. Using this approach, they measured H-Al distance of $2.5 \pm 0.3 \text{ \AA}$ for the BAS protons in ZSM-5, which resonates at 4.2 ppm [Figure 1B(i)]. A similar distance of $2.4 \pm 0.2 \text{ \AA}$ was obtained for protons resonating at the same isotropic chemical shift in deuterated ASA exposed to benzene [Figure 1B(ii)]. These NMR observations confirm the existence of BAS in ASA. Interestingly, for the silanol groups, negligible dephasing was observed for ZSM-5, whereas distances ranging from 4.2 to 5.7 \AA were found for ASA [Figure 1B(iii) and (iv)]. These distances are consistent with those predicted using molecular modeling for PBS in ASA.

In conclusion, Salvia *et al.* convincingly demonstrate, using solid-state NMR and selective isotope labeling, that besides PBS, ASA contains BAS similar to those found in zeolites, which can activate C-H bonds^[17]. The employed NMR experiments are expected to be useful in improving the acidity of ASA in a rational way. In particular, it will be beneficial to apply them to understand the structure of BAS in ASA with higher aluminum content, which exhibits higher catalytic activity toward H/D exchange^[19].

DECLARATIONS

Authors' contributions

The author contributed solely to this manuscript.

Availability of data and materials

Not applicable.

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Conflicts of interest

The author declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Professor Olivier Lafon earned his BSc in 2002 from Ecole Normale Supérieure de Lyon and his PhD in 2006 at the University of Paris-Saclay. Following his doctoral studies, he worked as a postdoctoral fellow at CEA Saclay. From 2007 to 2011, he served as an assistant professor at Centrale Lille. In 2010, he obtained his habilitation in 2010 at the University of Lille. Since 2011, he has been a professor at Lille, where he also leads the “NMR and inorganic materials” team in the UCCS research institute.

Professor Lafon received the Magnetic Resonance in Chemistry Award for Young Scientists from the Euromar scientific committee in 2013. In 2016, he was named a fellow of the Institut Universitaire de France (IUF). He currently directs the Lille high-field NMR facility, part of the INFRANALYTICS infrastructure, and coordinated the installation of a 1.2 GHz NMR spectrometer in Lille. Additionally, he leads the French network of research infrastructures in physical sciences and engineering and serves on the editorial board of the journal *Solid-State Nuclear Magnetic Resonance*.

His research focuses on advancing solid-state NMR spectroscopy to uncover unique insights into the structure-property relationships of materials, with applications in energy, bio-economy and health.