Atomic Description of the Interface between Silica and Alumina in Aluminosilicates through Dynamic Nuclear Polarization Surface-Enhanced NMR Spectroscopy and First-Principles Calculations

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ABSTRACT: Despite the widespread use of amorphous aluminosilicates (ASA) in various industrial catalysts, the nature of the interface between silica and alumina and the atomic structure of the catalytically active sites are still subject to debate. Here, by the use of dynamic nuclear polarization surface-enhanced NMR spectroscopy (DNP SENS) and density functional theory (DFT) calculations, we show that on silica and alumina surfaces, molecular aluminum and silicon precursors are, respectively, preferentially grafted on sites that enable the formation of Al(IV) and Si(IV) interfacial sites. We also link the genesis of Brønsted acidity to the surface coverage of aluminum and silicon on silica and alumina, respectively.

INTRODUCTION

Amorphous aluminosilicates (ASAs) are ubiquitous in catalysis and are used both as a catalyst and as a catalyst support for single sites, metal sulfides, and metal nanoparticles because they have high surface areas, combined with mild acidic properties alternative to zeolite in industrial reaction conditions. They are known to dehydrate ethanol to ethylene, as well as to catalyze the isomerization of m-xylene. They are also industrially used in refining technology to convert heavy fractions of crude oil and as supports for hydrotreating catalysts thanks to the tolerance of their acid sites to heteroelements containing organic molecules. They also show promising properties in the production of fine chemicals and the conversion of biomass.

Their activity arises from their acid/base properties. The presence of both aluminum and silicon atoms at the surface of the materials induces Brønsted acidity to the surface hydroxyls. However, the complex distribution of silicon and aluminum and the amorphous character of the material make the correlation between structure and activity very difficult to establish; the structure of the catalytically active sites are still a matter of debate. The original structural models of ASA proposed that the Brønsted acidity arises from protons compensating the electronic charge of the surface or from HO–Al groups close to silanol groups. Since these original pioneering works, numerous additional structural models have been proposed. Based on probe molecule adsorption, it has been suggested that the acidic sites are similar to those of zeolites, that is, bridging Si–OH–Al groups. In contrast to depositing aluminum or silicon precursors, coimpregnation yields sites of similar strength as zeolites. Other studies have concluded that the acidic sites are silanol groups in the vicinity of aluminum atoms (but not bridging the OH). In this case, the nature of Al atoms in the vicinity of the acidic groups is also a subject of discussion: tetrahedral Al(IV), five-coordinate Al(V), and unsaturated Al(III) sites have all been proposed. All these structural propositions are based on interpretation of complex spectral data. For instance, the assignments of OH infrared stretching frequencies have been debated. In particular, the vibrational properties of probes such as CO and pyridine are not
unambiguously specific to given ASA surface sites. Additionally, the numerous preparation routes give rise to a broad range of materials with varying structure, acidity, and active sites. Even the surfaces that are formed using well-defined methods are heterogeneous in nature. More recently, pseudobridging silanol groups have also been proposed to be active sites based on DFT calculations.

An efficient synthesis of ASA materials involves the controlled grafting of aluminum alkoxide or silicon alkoxide precursors onto a silica or alumina surface under anhydrous conditions at low temperatures, thus forming Al₂O₃ or SiO₂, and SiO₂ on Al₂O₃, (Si/Al₂O₃), respectively. This approach has the advantage of providing a homogeneous and regular deposition. The anhydrous conditions prevent the prehydrolysis of the precursor and inhomogeneous deposition. In addition, the amount of precursor grafted on the surface is mainly directed by the size of the alkyl chain of the precursor used. High Al and Si loadings may be achieved through successive grafting steps for both Al/SiO₂ and Si/Al₂O₃. The stoichiometric adsorption and further dehydration of ethanol enabled the quantification of the surface density of active sites. Even with a controlled deposition synthesis of ASA materials, Si/Al₂O₃ and Al/SiO₂ still have multiple types of Bronsted acid sites on their surface. Comparing these data to the catalytic activity for m-xylene isomerization revealed a moderate intrinsic acidity of these materials with respect to zeolites, Si/Al₂O₃ being the more reactive. Grafting of the silicon precursor occurred first on the (100) surface. Bronsted acidity only appeared upon grafting on the (110) surface.

While NMR spectroscopy is a valuable tool to obtain insights into the nature of Al and Si species on ASA, unambiguous identification of the most relevant surface sites has not been achieved yet, one reason being the small amount of surface sites combined with the low sensitivity of NMR. Dynamic nuclear polarization surface enhanced spectroscopy (DNP SENS) has recently been introduced to characterize materials and in particular their surfaces. In a DNP SENS experiment, the sample is impregnated with a small volume of a solution containing a persistent radical that acts as the DNP polarizing agent. Impregnation brings the solvent and DNP polarizing agent (usually a nitroxide biradical) into contact with the surface. DNP at low temperatures (ca. 100 K) is then used to enhance the polarization of protons of the solvent and surface functionality. The DNP enhanced proton polarization is then transferred to the surface heteronuclei by cross-polarization (CP) or other coherence transfer methods. For inorganic materials, signals from NMR active nuclei residing at the surface of the material are selectively enhanced since only the surface nuclei are in proximity to the protons of the solvent or surface functionalities. DNP SENS routinely provides sensitivity enhancements of 2 orders of magnitude, enabling NMR experiments that would normally require isotopic labeling or prohibitively long signal averaging periods.

Here, we apply DNP SENS for the detailed characterization of ASA materials prepared via controlled grafting approach, so as to provide an unambiguous characterization of the interface between silica and alumina for two well-defined series of samples: silica deposited on alumina (Si/Al₂O₃) and alumina deposited on silica (Al/SiO₂) materials. DNP NMR has recently been applied to characterize materials such as alumina, silica, and β-zeolite surfaces. Here DNP SENS allows sensitivity enhancements of several orders of magnitude, thus enabling the acquisition of natural abundance and dipolar heteronuclear correlation spectra, providing structural insight into the alumina/silica interface of these materials. Calculations of NMR signatures of surface sites of Si/Al₂O₃ on a aluminosilicate model by periodic density functional theory (DFT) calculations, which have proven to be efficient for the assignment of NMR spectra of various oxides, allow us not only to propose a structure for the interface between the alumina and the silica but also to propose structural models of the Bronsted acid sites of ASA.

### EXPERIMENTAL AND COMPUTATIONAL DETAILS

Samples were prepared by chemical liquid deposition (CLD) and exhibit different concentrations of SiO₂ on Al₂O₃ (Si/Al₂O₃) and Al₂O₃ on SiO₂ (Al/SiO₂) (Table 1). Si/Al₂O₃ samples were prepared by contacting excess tetraethyl-orthosilicate dissolved in dry toluene with alumina (resulting from calcination at 540 °C of Pural SB3, Sasol) in inert atmosphere (argon). After elimination of the unreacted precursor molecules, the samples were dried at 100 °C and further calcined at 500 °C under flow of air for 4 h. The 7.3 wt % of SiO₂ Si/Al₂O₃ sample was obtained after one grafting step; 12.0 and 17.1 wt % of SiO₂ Si/Al₂O₃ samples were obtained after completion of two and three grafting steps, respectively. In all cases, the final composition was determined by X-ray fluorescence spectroscopy. A similar procedure was applied for the preparation of the Al/SiO₂ samples. Aluminum isopropoxide dissolved in dry toluene was contacted with silica in inert atmosphere (silica gel beads from Grace). The amount of alumina precursor was adapted to obtain either 5.7 wt % of Al₂O₃ or 15.0 wt % of Al₂O₃ after one grafting step; 24.8 wt % Al₂O₃ was obtained after a second grafting step.

For DNP SENS experiments, the nitroxide biradical polarizing agents bCTbK and TEKPol were used. Incipient wetness impregnation with 1,1,2,2-tetrachloroethane (TCE) biradical solution with a concentration of 14 mM biradical was used to prepare the samples for DNP experiments. The impregnated samples were packed into sapphire rotors, and the sample was frozen at 100 K inside the low temperature 3.2 mm MAS probe head. Samples were typically subjected to multiple insert–eject cycles and left under an inert gas flow prior to insertion in order to reduce the amount of oxygen in the TCE solution and increase DNP enhancements. Experiments were performed with a 400 MHz (9.4 T)/263 GHz Bruker DNP system or a 600 MHz (14.1 T)/395 GHz Bruker DNP system. The sweep coil of the main magnetic field was set so that microwave irradiation occurred at the H² positive enhancement maximum of nitroxide biradicals. Standard ramped cross-polarization (CP) was then used to transfer polarization from the H nuclei to the nuclei of interest (²⁷Si or ²⁷Al). For H–²⁷Al CP experiments, a low ²⁷Al spin lock radiofrequency field less than 20 kHz was employed in order to maximize the efficiency of the CP transfers. Two-dimensional ²⁷Si–²⁷Al scalar correlation spectra were acquired with a refocused INEPT pulse sequence (Figure S1). ²⁷Si–²⁷Al dipolar correlation spectra were acquired with a dipolar refocused R³⁻ INEPT pulse sequence when first order rotary resonance recoupling (R³⁻) was employed to recouple ²⁷Si–²⁷Al dipolar couplings. In all cases, initial ²⁷Si magnetization was generated with H–²⁷Si CP with a 6 ms contact time. We also tested ²⁷Si–²⁷Al population-transfer-HMQC pulse sequences with detection of ²⁷Si to obtain scalar correlation spectra; however, the INEPT type sequences with ²⁷Al detection were found to provide superior sensitivity. ²⁷H–²⁷Al and ²⁷H–²⁷Si HETCOR experiments were performed with e-DUMBO22 homonuclear decoupling applied during the t₁ evolution period. The States-TPPI procedure was applied to achieve quadrature detection in the indirect.

### Table 1. Properties of Synthesized ASA Materials

| number of grafting cycles | wt % of Al₂O₃ grafted on SiO₂ (Al/SiO₂) | wt % of SiO₂ grafted on Al₂O₃ (Si/Al₂O₃) |
|---------------------------|----------------------------------------|----------------------------------------|
| 1                         | 5.7                                    | 7.3                                    |
| 2                         | 15.0                                   | 12.0                                   |
| 3                         | 24.8                                   | 17.1                                   |

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The resolution of the $^{29}$Al solid-state NMR spectra is greatly improved at higher magnetic field strength due to dipolar truncation, ensuring that only surface nuclei are detected. $^1$H DNP enhancements were measured with CP to $^{27}$Al ($\chi_{Al,CP}$) and were between 5 and 8 for the different samples at 600 MHz/395 GHz (Figure 1A, spectra a–c). Note that previous studies indicate that the overall sensitivity enhancement, compared with a dry sample at room temperature, is usually similar to the $\epsilon$ value under these conditions. $^1$H DNP enhanced $^1$H–$^{27}$Al CPMAS spectra were also acquired at 400 MHz/263 GHz and higher ($\chi_{Al,CP}$) signal enhancements between S1 and 80 were observed (Figure S3).

The resolution of the $^{29}$Al solid-state NMR spectra is greatly improved at higher magnetic field, as expected for quadrupolar nuclei such as $^{29}$Al. Therefore, our analysis of 1D spectra focuses on the high field spectra.

In all samples, three peaks centered around 6, 33, and 60 ppm are assigned, respectively, to hexa-coordinated Al(VI), penta-coordinated Al(V), and tetra-coordinated Al(IV) (Figure 1A). The spectra were acquired on a 400 MHz DNP spectrometer, with a recycle delay of 3.5 s. The pulse sequences used to acquire the 2D spectra are illustrated in Figure S1.

**RESULTS AND DISCUSSION**

Probing the Structure of Aluminum on SiO$_2$. The samples with increasing loadings of aluminum (i.e., 5.7, 15, and 24.8 wt % of AlO$_3$ on SiO$_2$ noted Al/SiO$_2$) were analyzed with $^1$H–$^{27}$Al cross-polarization magic angle spinning (CPMAS) solid-state NMR spectroscopy. Indirect $^1$H DNP coupled with CPMAS enables the selective enhancement of the NMR signals of the surface $^{27}$Al nuclei that are nearby to $^1$H nuclei of the surface hydroxyl groups and solvent molecules. Here a short contact time of 0.6 ms was employed in $^1$H–$^{27}$Al CPMAS experiments since it is well-known that with short contact times the CP experiment is very selective and only nuclei in close proximity to protons will be excited. CP transfers to more distant surface nuclei will also be less efficient due to dipolar truncation, ensuring that only surface nuclei are detected.

The DNP enhancement was measured by directly observing the $^1$H spectrum, since the acquisition of a $^{29}$Si CPMAS spectrum without DNP required too long for signal averaging. All spectra were acquired with a 12.5 kHz spinning frequency and a CP contact time of 0.6 ms for $^{27}$Al and 3.0 ms for $^{29}$Si. $^1$H–$^{29}$Si CPMAS spectrum of the starting silica is available Figure S7. (C) DNP SENS (400 MHz/263 GHz) scalar refocused INEPT (black traces/contours) and dipolar refocused $^R$-INEPT (red traces/contours). All spectra were acquired with a 12.5 kHz MAS frequency. Projections of the 2D spectra are shown along the horizontal and vertical axes. For dipolar correlation experiments, 420 total rotor cycles were used, while for scalar correlation experiments, 420 total rotor cycles of evolution were used. Spectra were acquired with between 16 and 80 scans per increment, 28 $t_1$ increments, and a rotor synchronized $t_2$ increment of 80 $\mu$s. Recycle delays were optimized for sensitivity and were between 3.8 and 5.0 s. The pulse sequences used to acquire the 2D spectra are illustrated in Figure S1.

The quadrupolar coupling constant ($\delta^{Q}$), the Gaussian distribution of the chemical shifts ($\Delta\delta_{iso}$), and the quadrupolar coupling constant ($\eta$) of $^1$H, $^{27}$Al, and $^{29}$Si were calculated. Tetramethylsilane (for $^1$H and $^{29}$Si) and $\alpha$-Al$_2$O$_3$ (for $^{27}$Al) were used as references for chemical shift calculations.

The density-of-states (DOS) was calculated for a Czek model implemented in DMat program in order to model the broad and featureless $^{27}$Al resonances characteristic of distributions of quadrupole and chemical shift parameters. The fits enabled the determination of the relative ratio of each species, the isotropic chemical shift ($\delta_{iso}$), the Gaussian distribution of the chemical shifts ($\Delta\delta_{iso}$), and the quadrupolar coupling constant.

Density functional theory (DFT) calculations were performed starting from the periodic ASA model previously established, according to a SiO$_2$/Al$_2$O$_3$ type, for $\theta_{OH} = 5.4$ nm$^{-1}$ and $\theta_{Al} = 6.5$ nm$^{-1}$. This model was obtained by calculating the interaction of silicic acid (silsilica acid and silica film) on a $\gamma$-Al$_2$O$_3$ model previously described by Digne et al. Molecular dynamics simulations revealed amorphization as well as mixing between the silica and alumina phases, by extraction of some aluminum atoms from the alumina layer to the silica one. The step-by-step simulation of hydration led to models of amorphization as well as mixing between the silica and alumina phases, by extraction of some aluminum atoms from the alumina layer to the silica one.

The one-dimensional $^{27}$Al DNP SENS CPMAS spectra were fit to a Czek model implemented in DMat program in order to model the broad and featureless $^{27}$Al resonances characteristic of distributions of quadrupole and chemical shift parameters. The fits enabled the determination of the relative ratio of each species, the isotropic chemical shift ($\delta_{iso}$), the Gaussian distribution of the chemical shifts ($\Delta\delta_{iso}$), and the quadrupolar coupling constant.

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coordinated Al(V), and tetra-coordinated Al(IV) aluminum sites, similarly to what is observed for γ-alumina, albeit with a larger component of Al(IV). In agreement with previous NMR measurements, the shape of the peaks in the spectra evolves as the concentration of alumina on SiO2 changes. We also note that as the Al loading increases, the intensity of the 27Al CPMAS spectra also substantially increases (Figure S3). The one-dimensional 27Al DNP SENS CPMAS spectra were fit to a Cžek model implemented in DMFit program to model the broad and featureless 27Al resonances characteristics of distributions of quadrupole and chemical shift parameters (Figure S4). The fits enabled the determination of the relative ratio of each species, the isotropic chemical shift, and the quardupolar constant (Table S1 and Figure S5). The fits show that for Al/SiO2, the relative amount of Al(V) (2%, 11%, and 17%) increases with higher aluminum loading.

For Al/SiO2, all of the 1D DNP enhanced 29Si CPMAS NMR spectra show a major peak centered at around −100 ppm and a reduced intensity “tail” at around −85 ppm (Figure 1B, spectra d–f). The major peak at −100 ppm indicates that most silicon atoms are present as Q4 sites. As the aluminum loading increases the intensity of the tail increases and moves toward more positive chemical shift. Silicon with multiple neighboring aluminum atoms or protons bound to the coordinating oxygen atoms should exhibit more positive chemical shifts (see next section, regarding Si/Al2O3 samples). It is indeed well-known from experiments on crystalline materials that substitution of aluminum atoms into neighboring tetrahedral sites around tetrahedral silica induces a positive displacement of the 29Si chemical shift. From solid-state NMR experiments performed on amorphous silica, it is also known that Si atoms with protons bound to coordinating oxygen atoms are also displaced to higher 29Si chemical shifts. Finally, we note that 1D 29Si CPMAS experiments and 2D 29Si–27Al INEPT-HETCOR experiments used 3 and 6 ms contact times, respectively, since these relatively long contact times gave the most signal. However, 29Si CPMAS spectra of 17.1% Si/Al2O3 acquired with contact times of 1–6 ms showed only minor variation in the observed 29Si chemical shifts with contact time (Figure S6). This suggests that even at relatively long contact times only the surface of the material is probed.

In addition, with increasing Al-loading, the relative number of Al(IV) sites decreases. We suspect that at high loading, the conversion of Al(IV) species into Al(V) is due to the increased ionicity of the framework, leading to preferred higher coordination number. Indeed, intrinsically, the Al−O bond is more ionic than the Si−O bond as expected from the respective electronegativity values of Al, Si, and O and the definition of ionicity given by Pauling. Simultaneously, the ratio of six-coordinate Al sites remains at around 60% of the total aluminum atoms.

To obtain direct insight into the bonding between Al and SiO2, DNP SENS 29Si–27Al INEPT was used to obtain two-dimensional 29Si and 27Al heteronuclear correlation (HETCOR) spectra of Al/SiO2 (Figure 1C, spectra g–i). We note that the 29Si–27Al correlation experiments are very challenging due to the low natural isotopic abundance of 29Si (natural abundance of 4.7%) and inefficient polarization transfer to/ from quadrupolar 27Al nuclei. Therefore, 2D 29Si–27Al correlation experiments were performed at 400 MHz/263 GHz where substantially higher DNP enhancements and NMR sensitivity were obtained. The HETCOR spectra were obtained with 29Si–27Al scalar couplings to selectively observe scalar coupled aluminum and silicon atoms linked by bridging oxygen (black traces). HETCOR spectra were also obtained with 29Si–27Al dipolar couplings by applying dipolar recoupling during the evolution period to observe both bonded and nonbonded but proximate aluminum and silicon atoms (red contours/traces). The scalar HETCOR spectra (black contours/traces) indicate that in all cases the silica tetrahedra are primarily bound to aluminum tetrahedra in Al/SiO2 (fits of the projected 27Al dimension for both scalar and dipolar spectrum are provided in the SI, see Figures S8 and S9 and Tables S2 and S3). The dipolar 29Si–27Al correlation spectra (Figure 1C, spectra g–i, red traces) show correlations between 29Si Q4 sites with 27Al(IV) and additional weak correlations between silicon and octahedral aluminum Al(VI) in all cases (Figure S9 and Table S3). This result is consistent with earlier NMR analysis on cogelled ASA samples with high silica content. The relative intensity of the latter correlations increases as the aluminum loading level is increased. As the dipolar correlation experiment gives correlations through space, the observed correlations to the octahedral Al-sites are very weak and likely arise from coupling to proximate nonbonded Al-octahedra. Note that at this stage, the correlation with Al(V) nuclei cannot be excluded but does not appear on the correlation plots probably due to low sensitivity of 29Si–27Al correlation experiments and the reduced resolution of the 27Al spectra at 9.4 T. We note that DNP enhanced 1H–27Al and 1H–29Si dipolar HETCOR spectra were also acquired (Figure S10 and S11). However, both the 1H–29Si and 1H–27Al HETCOR spectra generally show correlations to a very broad range of 1H chemical shifts (ca. 0.5 to 10 ppm), which likely reflects the diverse range of proton environments at the surface (hydroxyl, water, adsorbed solvent molecules, acidic protons, etc.). The most intense 1H peaks in the HETCOR spectra are centered around 4.5–5 ppm and ca. 6.2 ppm. These 1H chemical shifts likely correspond to adsorbed H2O and TCE solvent molecules, respectively. The 1H peaks in the HETCOR spectra are also rather featureless, which prevents useful structural information from being obtained.

In summary, the scalar and dipolar DNP SENS 29Si–27Al HETCOR spectra indicate that the majority of aluminum species that are bound to the silica surface via Si Q4 sites are Al(IV) and as the loading increases the number of Al(VI) proximate to the silica surface increases (Scheme 1).

**Probing the Structure of Silicon on Al2O3.** Si/Al2O3 prepared by the deposition of SiO2 on Al2O3 via a molecular condensation of the alkoxides is possible leading to the formation Al−O−Al-type species.
approach was also investigated by DNP SENS. $^1$H−$^{27}$Al CPMAS spectra were recorded for the Si/Al$_2$O$_3$ samples (Figure 2A, spectra a–c). Higher DNP enhancements of 7−20 were obtained for Si/Al$_2$O$_3$ compared with enhancements of 5−8 observed for Al/SiO$_2$ at 600 MHz/395 GHz. The larger enhancements observed for Si/Al$_2$O$_3$ samples (51−80 at 400 MHz/263 GHz) compared with Al/SiO$_2$ ($E_{\text{CP}}$ of 114−153 at 400 MHz/263 GHz) could reflect more suitable dielectric properties of alumina. However, other factors such as the degree of oxygen removal or interaction or aggregation of the radicals could also impact the observed DNP enhancements. Once again, three distinct resonances centered around 9, 36, and 65 ppm were observed in the $^1$H−$^{27}$Al CPMAS spectra and are assigned to Al(VI), Al(V), and Al(IV) aluminum atoms in agreement with DFT calculations (Table S4). Given the sensitivity of the $^{27}$Al NMR chemical shifts and quadrupole parameters to hydration and the challenge of accurately modeling water coordination/hydration of the surface, we did not consider the calculated $^{27}$Al NMR spectra.

Fits of the $^{27}$Al CPMAS spectra show that the relative ratio of the Al(VI)/Al(V)/Al(IV) sites is approximately 75:5:20 for all silica loading levels. There is no strong variation in the relative intensities of the different aluminum sites with increasing SiO$_2$ loading level (Figure S13 and Table S5). However, as the loading of SiO$_2$ is increased and the alumina surface becomes covered, the absolute intensity of the $^{27}$Al CPMAS spectra is observed to decrease (Figure S3). In addition, we may also expect a different intrinsic behavior of Al/SiO$_2$ and Si/Al$_2$O$_3$ interfaces. In Si/Al$_2$O$_3$, we expect that Al(V) sites result from the reconstruction–amorphization process as reported in ref 19; the rigid alumina framework imposes structural constraints and likely limits the formation of a large number of Al(V) even at high silica content. In contrast for Al/SiO$_2$, monomeric aluminum species deposited on the silica surface are intrinsically more flexible, thus allowing the formation of Al(V) from Al(IV) species (vide supra).

Once again, high-quality $^1$H−$^{29}$Si CPMAS spectra could be rapidly acquired (ca. 5 min for a one-dimensional spectrum). The DNP enhanced $^1$H−$^{29}$Si CPMAS spectra of Si/Al$_2$O$_3$ are shown for three different silicon loadings of 7.3, 12.0, and 17.1 wt % (Figure 2B, spectra d–f). The $^{29}$Si DNP SENS CPMAS spectra of Si/Al$_2$O$_3$ can be decomposed into three components at −83, −93, and −100 ppm (Figure S14 and S15). The calculated $^{29}$Si chemical shifts of the various surface sites are distributed between −78 and −99 ppm, consistent with the experimental observations. Applying Gaussian broadening to this distribution leads to the simulated spectrum reported in Figure 2B, trace g. The position of the maximum is enclosed between those of the experimental spectra of the 12% and 17.1% Si/Al$_2$O$_3$ sample. The DFT model is representative of a perfectly dispersed silica overlayer, without multilayers, which may explain the slightly different shape of the simulated spectrum compared with the experiment; the DFT simulated spectrum is slightly more intense at negative chemical shifts and less intense at the more positive chemical shift tail (Figure S16). Reducing the broadening for the simulated spectrum leads to a three-component spectrum (Figure S17), centered at around −80, −92, and −97 ppm. Excluding the Si atoms that do not have any hydrogen as second neighbors from the simulation does not affect the shape...
of the spectrum. All surface Si are likely observed since the contact time used for the $^1$H–$^{29}$Si CPMAS experiment is long (3 ms).

On the basis of DFT calculations, we can propose an assignment of the spectra of the Si/Al$_2$O$_3$ samples. Note however that the presence of various environments around similar $^{29}$Si (Figure 3), for example, various Si−O−Si and Si−O−Al angles and bond lengths, coordination numbers of Al atoms, presence of additional Al atoms noncovalently bonded but in close proximity to Si−O, will lead to a distribution of chemical shifts, only modeled in part here. In agreement with previous empirical assignments, based on the analysis of crystalline and amorphous aluminosilicates, both H and Al second neighbors are at the origin of the increase of the chemical shift of $^{29}$Si nucleus (Figure 4): the $Z_2$ site, corresponding to −78 ppm chemical shift, is surrounded by the highest number of Al neighbors ($n = 4$) together with a proton. Considering that all oxygen atoms surrounding a Si atom are 2-fold coordinated (as in silica), an empirical assignment (Figure S18) and model (Figure 4) can be drawn for each Si atom in silicates based on the number of H (i) and Al (n) neighbors, where the chemical shift of a specific Si site is positively shifted by $(10i + 5n)$ ppm from the chemical shift of pure SiO$_2$ ($Q_4$ sites, $\delta_{\text{iso}} = -110$ ppm) as a reference (see eq 1).

$$\delta_{\text{iso}}^{29}\text{Si}(i, n) = (10i + 5n) - 110 \text{ppm}$$

However, in the presence of alumina, a more ionic support than silica, oxygen atoms can adopt higher than 2-fold coordination. In alumina, the coordination number of oxygen atoms can be as high as four, so that higher coordination may be expected at the Si/Al interface. If we denote the environment of a given Si as $\text{Si}(n\text{Al}, i\text{H}, p\text{Si})$ to note the number of its second neighbors, DFT calculations show that $n + i + p$ can exceed four. This can be related to the so-called “O tricluster” suspected for aluminosilicate glasses. We can extend this concept to an “O tetracuster” on our silicate alumina surface model. This leads to a deviation (below 10 ppm) of the empirical model chemical shifts (Figure 4) since the $^{29}$Si chemical shift cannot be simply related to the nature and number of second neighbors.

To assign the experimental $^{29}$Si CPMAS NMR spectra, we compared the DFT calculated chemical shifts to the three experimental chemical shifts obtained from deconvolution of the $^{29}$Si CPMAS spectrum of 17.1% Si/Al$_2$O$_3$ (Figure 3). The $-93$ and $-100$ ppm peaks are clearly related to a higher number of Si atoms as second neighbors than the $-83$ ppm peak. The $-83$ and $-93$ ppm peaks correspond generally, but not necessarily, to a high number of Al as second neighbors (for example, $X_3$), since several H as second neighbors can also lead to increase in chemical shifts. Experimental evaluation of the peak intensities shows that at high silicon loading, Si species giving a signal around $-93$ ppm (and to a lower extent, $-100$ ppm) become dominant, whereas the $-83$ ppm signal vanishes, consistent with the existence of more numerous Si as second neighbors. This can be related to the formation of a SiO$_2$ multilayer and a pure silica network (Figure S14). At low loading, the $-83$ ppm peak increases dramatically, consistent with the first layer of silicate bonding directly to the surface of Al$_2$O$_3$.

Scalar two-dimensional $^{29}$Si−$^{27}$Al DNP SENS INEPT HETCOR spectra of Si/Al$_2$O$_3$ (Figure 2C, spectra h−j) show
that the silica tetrahedra are primarily bonded to the aluminum tetrahedra (decompositions of the projection of the $^{27}$Al dimension for both scalar and dipolar HETCOR spectra are given in Figures S8 and S9 and Tables S2 and S3). However, in the scalar HETCOR spectra, weak correlations to octahedral aluminum sites are observed, and the relative intensities of these correlations are constant (within the uncertainty of the measurement) with increasing loading of Si on alumina (Figure S8 and Table S2). This is consistent with the high intensity of the octahedral aluminum sites observed in the 1D $^{27}$Al CPMAS spectra of Si/Al$_2$O$_3$. The dipolar $^{29}$Si$-^{27}$Al HETCOR spectra of Si/Al$_2$O$_3$ show more intense correlations to octahedral aluminum sites and penta-coordinate aluminum, in particular for the lowest Si loading. The relative intensity of the correlations to the octahedral and penta-coordinate aluminum sites is also increased in Si/Al$_2$O$_3$ compared with the corresponding HETCOR spectra of Al/SiO$_2$ due to the presence of 6- and 5-fold coordination of aluminum sites on the alumina surface and therefore the close proximity with the $^{29}$Si nuclei (Figure S9 and Table S3). To explain this, we analyzed the Si to Al proximity in our DFT model (Figure S19). From this, we expect correlations with all types of Al atoms (IV, V, VI), but clearly the environment of Si is richer in Al(IV) than a priori expected from the structure of the alumina surface (on the (100) alumina orientation used for the simulation, no Al(IV) are exposed at the surface).$^{6,7}$ This can be interpreted as an Al(VI) to Al(IV) and Al(V) to Al(IV) conversion induced by silica. This conversion is likely driven by the higher degree of covalence of silica compared with alumina, which favors lower coordination numbers. This is in line with the higher Al(IV)/Al(VI) ratio observed as silica content increases in Al/$\gamma$-Al$_2$O$_3$, which was known from classical $^{27}$Al NMR.$^{18,37,38}$ Note that the Al(IV) giving signal in the $^{29}$Si$-^{27}$Al HETCOR spectra (Figures 1C and 2C) appears at slightly lower isotropic chemical shifts (62–66 ppm, Figure S9 and Table S3) than in the 1D DNP enhanced $^{27}$Al CPMAS NMR spectra (66–73 ppm, Figure S13 and Table S5). This can be related to the DFT results, which show that the isotropic chemical shift of Al(IV) is reduced when silicon is present as second neighbor (Figure 5). This is qualitatively comparable to observations from calculations on aluminosilicate glasses, even if the strength of the effect is different.$^{30}$ Note also that the $^{29}$Si nuclei detected in $^{29}$Si$-^{27}$Al HETCOR appear at more positive chemical shifts than those in the 1D $^{29}$Si CPMAS NMR spectrum. This is because Si sites that neighbor Al will give rise to more positive $^{29}$Si chemical shifts than Si near to only Si.

In summary, the 1D $^{27}$Al and $^{29}$Si and 2D $^{29}$Si$-^{27}$Al correlation spectra suggest that grafting of silica onto alumina primarily results in the formation of bonds between SiO$_4$ tetrahedra and tetrahedral Al(IV) sites; however, some SiO$_4$ tetrahedra are bonded to octahedral Al sites. Since SiO$_2$ is deposited onto Al$_2$O$_3$, most Si atoms will be proximate to the aluminum surface resulting in more intense correlations between Si and octahedral and penta-coordinated aluminum atoms. The observation of more negative $^{29}$Si chemical shifts with increasing Si loading level is also consistent with formation of a SiO$_2$ multilayer at higher loading level.

Taken together, the variation in the intensities of the DNP SENS 1D and 2D NMR with the loading levels can be used to propose some simple structural models (Scheme 2). On Si/

![Scheme 2](https://example.com/scheme2.png)

**Scheme 2. Representation of the Si/Al$_2$O$_3$ Interface Depicting Direct Bonding between Tetrahedral Aluminum Silicon Sites and Close Proximity of Octahedral Aluminum Sites**

$^X = \text{Al, Si, or H. Homocondensation of the alkoxides is possible leading to the formation Si–O–Si-type species.}$

Al$_2$O$_3$, the population of Al(IV) is more abundant than on Al/SiO$_2$ (from $^{27}$Al DNP SENS). Many Si nuclei are bonded to OH groups and are connected to Al(IV) as second neighbors, being also quite close to Al(VI) and Al(IV) species. This strong connection to Al(IV) atoms is linked to the locally strong covalence of ASA compared with alumina. As the silica loading increases, there is an overall increase in the intensity of signal with more negative chemical shifts. This suggests that increasing loading of SiO$_2$ results in the formation of a SiO$_2$ multilayer, likely a pure silica network. On the other hand, when Al is grafted onto silica in Al/SiO$_2$, the relative intensity of the tetrahedral sites is higher, due to the high covalence of the host matrix (silica). However, as the Al-loading increases, an Al$_2$O$_3$ overlay begins to form and relative ratio of tetrahedral to six-coordinate sites decreases to converge toward that of pure $\gamma$-alumina (3/1). Interestingly, the relative amount of penta-coordinated alumina sites at the surface increases with the grafting of alumina, suggesting that more defected alumina surface sites may result as the loading level is increased, thereby confirming previous propositions.$^{32}$

**Relation to Brønsted acidity.** The present NMR data, in particular the correlation experiments, yield new insight into the atomistic structure of the Brønsted acid sites of ASA materials. Table 2 quantifies the Brønsted acid sites.$^{36,31-33}$ On Al/SiO$_2$ samples, the occurrence of Si(IV)−Al(IV) connectivity as the aluminum loading increases is associated with a higher concentration of acid sites per Al atom on these samples.$^{33}$ Previous measurements of the concentration of Brønsted acid sites have shown that there are more Brønsted acid sites per deposited aluminum at low Al loading levels. The DNP SENS $^{27}$Al CPMAS spectra also show that there is an increase in the relative amount of Al(IV) sites at low loading levels. Taken together, these two results strongly suggest that the formation of Brønsted acid sites is related to the presence of Al/SiO$_2$ surface. This finding substantiates previous observations.$^{37}$

![Figure 5](https://example.com/figure5.png)

**Figure 5.** DFT calculated dependence on Al(IV) isotropic chemical shift as a function of the number of Si as second neighbors of Al. $\gamma$-Al$_2$O$_3$ serves as reference with no Si as second neighbors. In Al$_2$O$_3$−(OSi)$_x$ IV refers tetracoordinate aluminum and x to the number of (OSi) bound to Al.
Silicon connected to aluminum with higher coordination number would be inefficient in forming Bronsted acid sites.

The results on Al/SiO₂ materials show that the low coordination of the aluminum atoms and the presence of silica as a matrix are both crucial parameters for obtaining Bronsted acid sites in ASAs. Gathering such conditions by grafting silicon species on the Al₂O₃ surface is more difficult for two main reasons. On the one hand, the coordination of the aluminum atoms populating the Al₂O₃ surface is on average closer to six than to four, higher than that of the first aluminum species deposited in Al/SiO₂ samples. On the other hand, a significant amount of deposited silicon species is required so as to change the covalence of the surface aluminum species in such a way that it induces the formation of reactive sites. Hence the number of Bronsted acid sites per exposed aluminum atom in Si/Al₂O₃ samples increases with the silica loading and consequent coverage of aluminum surface species.

Hensen et al.²⁰ categorized the acid sites of ASAs in two main types, the strongest ones being bridging acid sites such as in zeolites and the milder ones being specific to ASAs with different structures. Experimental and computational data combined suggest that the structures of the acid sites of ASAs are bridging hydroxyls (Scheme 3). According to calculations, such species can be protonated by basic probe molecules (B) such as lutidine, by closing the Si—O···Al bridge, yielding Si—O—Al anionic species and BH⁺, in agreement with ref ¹⁷, ⁴⁰, ⁹³ Moreover, the intrinsic protonation and cracking abilities of such PBS sites have recently been compared with bridging acid sites of a zeolite in DFT calculations, and these specific structures would account for the milder acidity of PBS and corroborate the main role of the interaction between the alumina support and deposited silicon species.⁹⁸ In the present work, on the basis of the NMR spectra, we suggest that the acceptor Al atom is likely in tetrahedral coordination and that the silicon bearing the silanol is covalently bonded to other Al(IV) ions (Scheme 3). However, all PBS sites are covalently connected to only Al(VI) and Al(V) in the DFT model discussed here, due to the high aluminum content. While it is hard to make an unambiguous prediction of the ²⁹Si NMR chemical shift for sites depicted in Scheme 3, the two PBS sites, V₁ and Z₂ in Figure 3, can be considered as prototypical examples: they are characterized by very distinct calculated chemical shifts of −96 and −78 ppm, respectively. This large difference of calculated chemical shifts for similar species shows that ¹D NMR cannot be used to identify the Bronsted acid sites of ASA. In contrast, NMR correlation experiments, which probe Al(IV) to Si(IV) proximity, a requirement for Bronsted acidity, are therefore better suited to characterize such species.

## CONCLUSIONS
Combining DNP SENS NMR, including 2D scalar and dipolar ²⁹Si—²⁷Al INEPT, and DFT calculations on ASA materials has allowed for a detailed atomic level description of (i) the connectivity between Si and Al nuclei on ASA surfaces, as a function of their coordination number and local environment, and (ii) structural insight into the nature of Bronsted acid sites, which unifies the behavior of solids obtained by grafting either Al on silica or Si on alumina.

On silica and alumina surfaces, molecular Si and Al precursors are preferentially grafted as “(IV)-to-(IV)“-coordinated mixed layer: the deposited silicon species are preferentially attached to Al(IV) sites issued from Al atoms of various coordinations of y-alumina, with strong Si(IV)—Al(IV) connectivity. Similarly, the first deposited aluminum species on silica in Al/SiO₂ are Al(IV) tetrahedrally coordinated species. This specific surface site connectivity eventually enables the formation of Bronsted acid sites. Such acid sites may be formulated as bridging hydroxyls in connection with Al(IV) species, such as pseudo-bridging silanol in Al/SiO₂. While an atomic level description of the interface of ASAs remains complex because each preparation technique makes a unique structure, the present study lays the foundation for the determination of the structure of the Bronsted active sites in the large family of aluminosilicates with the ultimate goal to establish structure–activity relationships and to use more rational development of solid acid catalysts.

## ASSOCIATED CONTENT

### Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06134.

Refocused INEPT pulse sequence, a compilation of ²⁹Si and ²⁷Al NMR spectra and their fits, and details on the DFT calculations (PDF)

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**Table 2. Coverage by Aluminum Species and Surface Density of Bronsted Acid Sites**

| sample            | Bronsted acid sites (nm⁻²) | Bronsted acid sites per Al atom (× 10⁻⁴, Al exposed)³¹,³³ |
|-------------------|-----------------------------|----------------------------------------------------------|
| 5.7% Al₂O₃/SiO₂    | 0.20                        | 15.4                                                     |
| 15% Al₂O₃/SiO₂     | 0.39                        | 6.7                                                      |
| 24.8% Al₂O₃/SiO₂   | 0.52                        | 7.3                                                      |
| 7.3% SiO₂/Al₂O₃   | 0.04                        | 0.5                                                      |
| 12% SiO₂/Al₂O₃    | 0.11                        | 1.5                                                      |
| 17.1% SiO₂/Al₂O₃  | 0.19                        | 5.2                                                      |

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**Scheme 3. Proposal for a Possible Structure of Bronsted Acid Sites on ASA (Si/Al₂O₃): Pseudo-Bridging Silanol in Connection with Al(IV) Species**

![Diagram](image-url)

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REFERENCES

(1) Corma, A. Chem. Rev. 1995, 95, 559.
(2) Busca, G. Chem. Rev. 2007, 107, 5366.
(3) Perez-Ramirez, J.; Christensen, C. H.; Egeblad, K.; Christensen, C. H.; Groen, I. J. Catal. 2008, 273, 2530.
(4) Stebbins, J. F.; Xu, Z. Nature 1997, 390, 60.
(5) Moses, A. W.; Raab, C.; Nelson, R. C.; Leifeste, H. D.; Ramsahye, N. A.; Chattopadhyay, S.; Eckert, J.; Chmelka, B. F.; Scott, S. L. J. Am. Chem. Soc. 2007, 129, 8912.
(6) Motokura, K.; Tada, M.; Iwasawa, Y. J. Am. Chem. Soc. 2007, 129, 9540.
(7) Alphazan, T.; Bonduelle-Skrzypczak, A.; Legens, C. I.; Gay, A.-S.; Boudene, Z.; Girleaun, M.; Ersen, O.; Copéret, C.; Raybaud, P. ACS Catal. 2014, 4, 4320.
(8) Bertoncini, F.; Bonduelle-Skrzypczak, A.; Francis, J.; Guillon, E. Catalysis by Transition Metal Sulphides: From Molecular Theory to Industrial Application; Raybaud, P.; Toulohoat, H., Eds.; Technip: Paris, 2013; Chapter 3.4, p 609.
(9) Theulieuc, C.; Maraval, A.; Veyre, L.; Copéret, C.; Soulouvong, D.; Basset, J.-M.; Sunley, G. J. Am. Chem. Soc. Int. Ed. 2007, 46, 2288.
(10) Wetkamp, J. ChemCatChem 2012, 4, 292.
(11) Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. Science 2010, 327, 1110.
(12) Hahn, M. W.; Copeland, J. R.; van Pelt, A. H.; Sievers, C. ChemSusChem 2013, 6, 2304.
(13) Marcilly, C. I. Catal. 2003, 216, 47.
(14) Hensen, E.; F; J. Catal. 1998, 179, 581.
(15) Grégoire, G.; Montouillott, V.; Vichon, A.; Unger, L.; Cseri, T.; Maugé, F. J. Catal. 2006, 210, 15172.
(16) Chiralt, C.; Raybaud, P. Angew. Chem. Int. Ed. 2009, 48, 2891.
(17) Podvalov, D. G.; van Veen, J. A. R.; Rigutto, M. S.; Hensen, E. J. M. Chem. Commun. 2010, 46, 3466.
(18) Thomas, C. L. Ind. Eng. Chem. 1949, 41, 2564.
(19) Tamele, M. W. Discuss. Faraday Soc. 1950, 8, 270.
(20) Hansford, R. C. Ind. Eng. Chem. 1947, 39, 849.
(21) Xu, B.; Sievers, C.; Lercher, J. A.; van Veen, J. A. R.; Giltay, P.; Prins, R.; van Bokhoven, J. A. I. Phys. Chem. C 2007, 111, 1209.
(22) Huang, J.; van Vegen, N.; Jiang, Y.; Hunger, M.; Baiker, A. Angew. Chem. Int. Ed. 2010, 49, 7776.
(23) de Boer, J. H. Discuss. Faraday Soc. 1971, 52, 109.
(24) Blonski, S.; Gorotlalimi, S. H. J. Phys. Chem. 1996, 100, 2201.
(25) Hwang, C.-P.; Yeh, C.-T. J. Am. Chem. Soc. 2010, 132, 13249.
(26) Bertoncini, F.; Bonduelle-Skrzypczak, A.; Francis, J.; Guillon, E. Catalysis by Transition Metal Sulphides: From Molecular Theory to Industrial Application; Raybaud, P.; Toulohoat, H., Eds.; Technip: Paris, 2013; Chapter 3.4, p 609.
(27) Theulieuc, C.; Maraval, A.; Veyre, L.; Copéret, C.; Soulouvong, D.; Basset, J.-M.; Sunley, G. J. Am. Chem. Soc. Int. Ed. 2007, 46, 2288.
(28) Hansford, R. C. Ind. Eng. Chem. 1947, 39, 849.
(29) Xu, B.; Sievers, C.; Lercher, J. A.; van Veen, J. A. R.; Giltay, P.; Prins, R.; van Bokhoven, J. A. I. Phys. Chem. C 2007, 111, 1209.
(30) Huang, J.; van Vegen, N.; Jiang, Y.; Hunger, M.; Baiker, A. Angew. Chem. Int. Ed. 2010, 49, 7776.
(31) Bertoncini, F.; Bonduelle-Skrzypczak, A.; Francis, J.; Guillon, E. Catalysis by Transition Metal Sulphides: From Molecular Theory to Industrial Application; Raybaud, P.; Toulohoat, H., Eds.; Technip: Paris, 2013; Chapter 3.4, p 609.
(32) Theulieuc, C.; Maraval, A.; Veyre, L.; Copéret, C.; Soulouvong, D.; Basset, J.-M.; Sunley, G. J. Am. Chem. Soc. Int. Ed. 2007, 46, 2288.
(33) Hansford, R. C. Ind. Eng. Chem. 1947, 39, 849.
(34) Xu, B.; Sievers, C.; Lercher, J. A.; van Veen, J. A. R.; Giltay, P.; Prins, R.; van Bokhoven, J. A. I. Phys. Chem. C 2007, 111, 1209.
(35) Huang, J.; van Vegen, N.; Jiang, Y.; Hunger, M.; Baiker, A. Angew. Chem. Int. Ed. 2010, 49, 7776.
(36) de Boer, J. H. Discuss. Faraday Soc. 1971, 52, 109.
(37) Bertoncini, F.; Bonduelle-Skrzypczak, A.; Francis, J.; Guillon, E. Catalysis by Transition Metal Sulphides: From Molecular Theory to Industrial Application; Raybaud, P.; Toulohoat, H., Eds.; Technip: Paris, 2013; Chapter 3.4, p 609.
