Surface Selective $^1$H and $^{27}$Al MAS NMR Observations of Strontium Oxide Doped $\gamma$-Alumina

Surface binding sites of strontium oxide on $\gamma$-alumina identified for the first time

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High-surface area $\gamma$-alumina is industrially used as a catalyst support. Catalytically active elements are doped onto the support, where they can bind to AlO$_4$, AlO$_5$ or AlO$_6$ sites on the surface. Pretreating the surface with alkaline earth oxides can alter the availability of these surface sites, hence affecting the catalytic activity. The surface binding sites of strontium oxide (SrO) on $\gamma$-alumina were previously unknown. Direct $^{27}$Al magic angle spinning nuclear magnetic resonance (MAS NMR) could not detect AlO$_5$ sites at 9.4 T, so $^1$H–$^{27}$Al cross-polarisation (CP) MAS NMR was used to preferentially select the surface environment signals. We directly observed the three surface environments on dehydrated $\gamma$-alumina as a function of SrO impregnation up to 4 wt% SrO. We found that Sr$^{2+}$ preferentially binds to AlO$_5$ and AlO$_6$ surface sites.

$^1$H MAS NMR revealed SrO impregnation causes a reduction in the terminal (~0.3 ppm) and bridging (2.2 ppm) hydroxyl environments, as well as the promotion of a new peak in between these sites, at 0.5 ppm. By using $^1$H–$^{27}$Al CP/MAS NMR the relative proportions of surface sites on $\gamma$-alumina can be determined, allowing an optimal level of SrO doping that can saturate all the AlO$_5$ sites. Importantly, this provides a method of subsequently depositing catalytically active elements on just the AlO$_4$ or AlO$_6$ sites, which can provide a different catalytic activity or stability compared to the AlO$_5$ binding site.

1. Introduction

Over 80 million tons of alumina are produced annually, which is used industrially for the production of aluminium and in applications requiring high melting point, excellent mechanical strength, electrical resistivity or chemical inertness (1). There are several polymorphs of alumina and the thermal transformations between them are well known (2). $\gamma$-Alumina in particular has a favourable combination of high surface area, pore size distribution and acid/base characteristics, which makes $\gamma$-alumina a common industrial catalyst support (3).

Specific applications of $\gamma$-alumina in catalysis include as a binder for zeolite catalysts in fluid catalytic cracking (4), as iron/copper/potassium (FeCuK) support for Fischer-Tropsch catalysis (5) and as a platinum support for dehydrogenation of jet fuel (6) or carbon monoxide oxidation (7). Three-way catalysts (TWC), which are widely used on gasoline engines to reduce CO, nitrogen oxides (NOx) and hydrocarbon emissions, include $\gamma$-alumina as part of the mixed oxide support because of its high surface area and relatively good thermal stability under hydrothermal conditions (8, 9). Barium oxide (BaO) and lanthana are commonly...
used as stabilisers for alumina in TWC. An additional advantage of adding alkaline earth oxides to γ-alumina is the improvement of NOx storage for TWC (10, 11). Thus, the investigation of SrO structure on the surface of γ-alumina is one of practical importance. The matter is complicated as despite the massive production and industrial use of γ-alumina, the surface topography of γ-alumina is still under debate (12). Nevertheless, there is clear agreement that three main aluminium coordination environments exist on the surface: AlO4, AlO5 and AlO6.

Solid-state nuclear magnetic resonance (SSNMR) of alumina is informative as the aluminium environments give distinct 27Al peak positions; AlO4 ≈ 60 ppm, AlO5 ≈ 30 ppm and AlO6 = 0 ppm. As 27Al is a quadrupolar nucleus (13), the observed chemical shifts vary as a function of magnetic field strength, but remain distinct at all high fields (14). Studies on γ-alumina have been reported for the past 25 years, both using direct 27Al NMR (15–17) as well as using 1H to 27Al CP NMR (12, 18, 19). More recently, dynamic nuclear polarisation (DNP) has been used to enhance the 27Al NMR signals from the surface of γ-alumina, calculations have shown that the 27Al CP signal is from the very first surface layer or primostrato (20, 21). This is in agreement with a deuteration experiment that concluded the CP signal does not come from interstitial or sub-surface hydrogens (18). Some computational studies disagree as the surface 27Al nuclei are reported to have a large quadrupolar coupling, which broadens the 27Al signal and makes CP ineffective (16, 22). However, the models used for these calculations did not account for surface rearrangement, which will favour less strained symmetric environments, as has been seen in alumina (23).

Penta-coordinated aluminium environments, i.e., AlO5, exist on the surface of γ-alumina and can be observed using CP NMR (19, 21) or directly using high-field NMR measurements (24–27). Interestingly, little or no AlO5 was observed by DNP NMR despite being a surface enhanced measurement, presumably because the alumina was mixed with an aqueous solution that reacted with the AlO5 sites (20, 21). These AlO5 sites have been shown to be the anchoring point for platinum oxide (26). Concerning alkaline earth oxide doping, AlO5 has a one-to-one correlation against the number of BaO molecules impregnated on to γ-alumina (27). Hence, the surface AlO5 sites are of great interest to the catalyst scientist.

Although no hydrogen atoms exist in the bulk of γ-alumina, the surfaces \{111\}, \{110\} and \{100\} are terminated by hydroxyl groups. Knözinger and Ratnasamy extended the earlier work of Peri who identified five types of hydroxyl environment on a hydroxylated ideal γ-alumina surface (28, 29). This model was again extended by Tsyganenko and Mardilovich who added a sixth environment, reproduced in Figure 1. (Note that in this article we refer to AlIV as AlO4).

Many workers have reported 1H NMR spectra of γ-alumina and attempted to assign peaks to specific hydroxyl environments. As-received γ-alumina contains a significant amount of physisorbed water throughout its porous structure, which overwhelms the 1H NMR signal from the surface hydroxyls. Thus, all 1H NMR experiments on γ-alumina must necessarily be performed after the sample has been heated above 250ºC to remove water and consequently the γ-alumina will be partially dehydroxylated. This is significant as penta-coordinated environments such as OH5, OH65 and OH665, will be present that require assignment despite not having a particular Knözinger and Ratnasamy type (30–32). One limitation of this 1H NMR technique is the requirement for drying, as the environments formed might not be present during, for example, a subsequent incipient wetness treatment to load the support with a catalytically active species.

Initial studies reported peaks of around −0.3 ppm, 2.4 ppm, 4.0 ppm and higher, which were assigned to the most basic OH group (type Ib), a more acidic group (type II), the most acidic (type III) and finally hydrogen-bonded protons, respectively (33, 34). Later studies appreciated the presence of AlO6 with assignments of −0.2 ppm to −0.5 ppm: OH4, 1.5 ppm to 2.5 ppm: OH45,

![Diagram of six surface hydroxyl environments on γ-alumina](http://dx.doi.org/10.1595/205651316X690943)

Fig. 1. Six surface hydroxyl environments that can exist on γ-alumina, labelled by Knözinger and Ratnasamy type and Tsyganenko and Mardilovich OH\(^5\) nomenclature.
2.5 ppm to 4.0 ppm: OH\textsuperscript{nnn} and higher shifted hydrogen-bonded protons (12, 35, 36). These assignments are in agreement with the earlier studies, clearly showing the trend of increasing chemical shift going from terminal (μ\textsuperscript{1}) to bridging (μ\textsuperscript{2}) to μ\textsuperscript{3} OH environments.

To date, there have been no reports on the surface aluminium environments of any alumina that has been impregnated by SrO. The catalytic activity of a γ-alumina support, doped with an active species, will be affected by strontium doping that causes the surface environments to rearrange. For example, by blocking the AlO\textsubscript{5} sites, an active species can anchor to a weaker aluminium binding site (AlO\textsubscript{4}/AlO\textsubscript{6}), thus changing the catalytic activity. Accurate understanding of alkaline earth oxides on the surface of γ-alumina must explain changes in the aluminium coordination populations as well as ¹\textsuperscript{H} NMR assignments. The scope of this article is to present novel NMR spectra on a strontium alumina system and suggest possible surface environments to explain those spectra. These hypotheses could be tested by future infrared measurements as well as ab initio calculations.

2. Experimental Results

1 wt%, 2 wt% and 4 wt% SrO on γ-alumina (Sasol) samples were prepared by incipient wetness impregnation using strontium nitrate (Alfa Aesar) dissolved in sufficient water. Following addition of the nitrate solution to the alumina, the samples were dried at 105°C before being calcined at 500°C for two hours.

Powdered samples were dried under vacuum at 350°C overnight, before being packed in air-tight zirconia rotors under an inert atmosphere and were spun at 14 kHz in a static magnetic field strength of 9.4 T. A widebore Bruker 4 mm broadband (BB)/¹\textsuperscript{H} MAS probe was used. Spectra were normalised by mass and number of scans and all acquired on a Bruker Avance III console using TopSpin 3.1 software. All experiments used a 2 s recycle delay.

¹\textsuperscript{H} spectra were acquired (256 scans) with one rotor period spin echo experiment (37) and referenced to the low-ppm peak of adamantane-d\textsubscript{16} at 1.73 ppm. Pulse lengths were 3 μs (90°) and 6 μs (180°) at ν\textsubscript{RF} = 83 kHz. ²⁷\textsuperscript{Al} spectra were referenced to yttrium-aluminium garnet (YAG) AlO\textsubscript{6} at 0.8 ppm (38). Direct acquisition (128 scans) used a 1.5 μs (<30°) pulse at ν\textsubscript{RF} = 50 kHz. CP spectra (7168 scans) used a 1.5 ms contact pulse. ²⁷\textsuperscript{Al} ν\textsubscript{RF} = 12 kHz and ¹\textsuperscript{H} ν\textsubscript{RF} = 36 kHz to satisfy the Hartmann-Hahn condition (39, 40). The low radio-frequency (RF) field gives selective spin-locking of the central transition (m = ½ to −½), but under MAS, lineshapes will be distorted (41, 42). Proton decoupling did not improve resolution and was not used.

2.1 ²⁷\textsuperscript{Al} Nuclear Magnetic Resonance

Directly acquired ²⁷\textsuperscript{Al} spectra of the bulk are given in Figure 2. Peaks corresponding to AlO\textsubscript{4} and AlO\textsubscript{6} were clearly visible, present in an approximately 1:2 ratio by integration, which does not account for spinning sideband intensity. The contribution of surface AlO\textsubscript{5} environments was undetectably small against the background bulk signals. After normalising by sample mass, there was no significant variation in the bulk aluminium environments. This indicates that the SrO impregnation did not affect the structure of the γ-alumina nor form a strontium-aluminate phase.

Primostrato ²⁷\textsuperscript{Al} CP spectra are given in Figure 3. Focusing initially on the undoped alumina; in contrast to the bulk spectra, the presence of AlO\textsubscript{5} was clearly visible. The ratio of AlO\textsubscript{4} and AlO\textsubscript{6} sites showed a preference for AlO\textsubscript{6} sites at the surface of γ-alumina. Although CP NMR spectra are not quantitative, the quadrupolar parameters of AlO\textsubscript{4} and AlO\textsubscript{6} were similar enough to allow for qualitative comparison. This is strong evidence that a surface rearrangement has taken place, i.e., the surface structure is not the same as the bulk structure.

The effects of SrO doping are also pronounced, with variation seen in all three types of aluminium environment. With the addition of 1% SrO there was an enhancement of AlO\textsubscript{4} signal, no change to the AlO\textsubscript{5} signal and a reduction in AlO\textsubscript{6} signal. For the γ-alumina with 2% SrO the AlO\textsubscript{4} signal was enhanced even more.
whilst there was a reduction in AlO₅ and AlO₆ signals. This trend continued for the 4% SrO sample. Generally, a reduction in CP²⁷Al signal could be caused by several factors: (a) an actual physical reduction in that type of environment; (b) the removal of nearby hydrogen to that environment (as the magnetisation is transferred to aluminium from hydrogen) or (c) a distortion of the aluminium site symmetry causing extreme quadrupolar broadening and rendering the signal ‘invisible’. The likelihood of these different factors occurring upon Sr doping will be discussed below.

2.2 ¹H Nuclear Magnetic Resonance

The processed spectra are given in Figure 4. For the undoped γ-alumina three main environments were seen, in agreement with previous studies (12, 33, 35). These were assigned as HO-µ¹ at −0.3 ppm, HO-µ² at 2.2 ppm and HO-µ³ at 4.3 ppm. Hydrogen-bonded environments also existed at higher chemical shifts, but in a lesser amount to the main environments. Systematically doping γ-alumina with SrO produced an additional peak at 0.5 ppm whilst simultaneously reducing the terminal and bridging hydroxyl environments at −0.3 ppm and 2.2 ppm, respectively. The hydrogen-bonded and HO-µ³ environments appeared unaffected by the SrO doping.

As there are several specific types of surface hydroxyl group and the peaks appeared asymmetric, the spectra were deconvolved. At least seven peaks were required to obtain a good fit, although the lack of resolution meant that such a fit was ambiguous. Two of the fitted spectra are shown in Figure 5. The purpose of the fits is to show that a full structural model of the surface of γ-alumina must account for at least seven hydroxyl environments. Also, the fits show approximately how the various environments change upon doping with SrO.

Further experiments were performed to help assign the additional peak at 0.5 ppm. A strontium hydroxide (Sr(OH)₂) species was ruled out, as measurements on this material gave much higher chemical shifts. Both X-ray photoelectron spectroscopy (XPS) and chemical testing (addition of acid caused carbon dioxide evolution) indicated the presence of strontium carbonate (SrCO₃), which being energetically stable, is a likely surface species.

Hence, the 4% SrO γ-alumina sample was dosed with CO₂ overnight to promote a carbonate environment. The resulting ¹H NMR spectrum is given in Figure 6. A loss
of intensity for the HO-μ¹ environment was observed and a new peak at 5.2 ppm was gained. This peak corresponds to an aluminium carbonate OH signal (12). Clearly the presence of Sr did not inhibit the adsorption of CO₂ on γ-alumina but significantly, this mechanism did not occur for atmospheric amounts of CO₂. This suggests the 0.5 ppm peak was not related to carbonate species.

In conclusion, SrO doping systematically affected the proton environments on γ-alumina, modifying the previously identified HO-μ¹ and HO-μ² hydroxyls and producing a new peak at 0.5 ppm. Although this new environment has not been identified, the correlation with SrO doping suggests the hydroxyls are proximate to some strontium compound, which will be discussed below.

3. Discussion

We first discuss the changes in the ²⁷Al CP/MAS NMR spectra upon SrO doping shown in Figure 3. The addition of SrO appears to preferentially replace the hydroxyls located at AlO₅ and AlO₆ sites. This preference could be because of the energetic favourability of Sr²⁺ towards the more electronegative AlO₅ and AlO₆ sites. Consequently, the reduction in CP signal from the AlO₅ and AlO₆ sites is simply because of a reduction in nearby protons that the magnetisation would otherwise be transferred from. Whether Sr is present as isolated atoms or in SrO clusters is unclear from the ²⁷Al NMR.

An increase in AlO₄ CP signal upon SrO doping is harder to explain. One possibility for enhanced signal is to introduce additional hydroxyls. However, directly bonded hydroxyls would increase coordination causing the signal to appear elsewhere, which has not been observed. Another possibility is that the presence of SrO promotes a structural rearrangement of higher coordination aluminium to AlO₄. This would be the opposite of condensation reactions typically seen when dopants are added to alumina and a plausible mechanism has not been forthcoming (43).

Two possibilities remain. One is that the addition of SrO causes AlO₄ sites to become more symmetric. This reduces their quadrupolar broadening giving rise to a more effective magnetisation transfer from ¹H to ²⁷Al. Thus, previously ‘invisible’ AlO₄ sites appear in the primostrato spectra when SrO is added. Further experiments at multiple fields or using multiple quantum magic angle spinning (MQMAS) could be performed to determine the quadrupolar parameters and test this possibility. The other possibility is that SrO, replacing AlO₂ and AlO₆ hydroxyls, could then prohibit the fast exchange of protons across the surface, facilitating CP from the remaining protons on AlO₄ sites (16).

Next we discuss the changes in the ¹H spectra upon SrO doping shown in Figure 4. As mentioned above, the peak at 0.5 ppm grew in proportion with the quantity of SrO doped, which suggests these hydroxyls are proximate to some Sr compound. Additional experiments have ruled out the assignment of Sr(OH)₂ or SrCO₃. Furthermore, the chemical shift is in between the typical terminal and bridging environments. Combined with the unchanging environments above 4 ppm, these findings lead us to conclude that the peak at 0.5 ppm is from a shifted OH₅ or OH₆ site.

As the most reactive/electronegative OH₅, OH₆, OH₅₆ and OH₆₆ environments have most likely been replaced by SrO, these are probably not an accurate assignment for the 0.5 ppm peak. The presence of an OH₄₄ environment is generally energetically unfavourable, so this too can be ruled out. This leaves us with modified OH₄ and/or OH₄₆ environments.

Further evidence that favours the assignment of OH₄ comes from the CO₂ dosing results shown in Figure 6. As it has been shown that CO₂ preferentially goes...
to the OH$^4$ sites (12), the dramatic intensity loss of the 0.5 ppm peak strongly suggests this was a OH$^4$ environment.

4. Conclusion

The need for further research into the nature of the Sr environment and more comprehensive $^1$H peak assignments, is clearly indicated. This could be achieved through higher resolution $^1$H NMR experiments as well as $^1$H–$^{27}$Al correlation experiments. NMR data can be combined with infrared measurements to probe the hydroxyls. Raman microscopy and transmission electron microscopy (TEM) may also be used to elucidate the Sr environment. Ideally, the experimental data can all be used to create accurate surface models for density functional theory calculations to further explain the mechanisms at work in this system.

In conclusion, $^1$H–$^{27}$Al CP MAS NMR has shown that doping $\gamma$-alumina with SrO covers AlO$_5$ and alters the surface AlO$_4$:AlO$_6$ ratio. $^1$H MAS NMR revealed SrO impregnation caused a loss or shifting, of the terminal and bridging hydroxyl environments, with a new peak at 0.5 ppm hypothesised to be a modified OH$^4$ environment. These changes to surface chemistry will strongly affect where catalytically active metals are subsequently deposited. Such tunability for a common industrial catalyst support, like $\gamma$-alumina, is of great interest to the catalyst scientist.

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References

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