Catalytic Decomposition of Perfluorinated Carbons (PFCs) During the Aluminium Smelting Process

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Abstract

Perfluorinated carbons (PFCs) are potent greenhouse gases that are formed in the primary aluminium industry when the alumina (Al_2O_3) concentration in the reduction cell is depleted. Hydrolysis on the surface of an Al_2O_3-based catalyst is potentially a viable method of PFC breakdown with the advantage of compatibility with the current process. The waste heat within the aluminium cell itself can be used to reach reaction temperatures for the catalytic process to occur, the spent catalyst can be easily disposed by feeding to the reduction cell, and the hydrogen fluoride (HF) byproduct of the catalytic decomposition can be captured using conventional dry-scrubbing techniques.

This study takes an in-depth look at tuning the surface chemistry of the alumina-based catalyst to maintain high-efficiency of PFC breakdown in a HF-rich environment which will poison the catalyst surface over time. Maximizing Lewis acid sites on the catalyst surface is believed to be the key to optimization. Characterization methods have provided quantitative and qualitative data to determine which catalyst is best suited for PFC decomposition.

Keywords: Perfluorinated carbons, Alumina catalyst, Surface acidity, Al NEXAFS, Primary Aluminium production

1. Introduction

Perfluorinated carbons (PFCs) are highly stable compounds produced as a byproduct in primary aluminium smelting when the alumina concentration in the reduction cell is depleted and voltage rise causes the decomposition of the electrolyte. PFCs are also potent greenhouse gases that absorb infrared radiation in the atmosphere where naturally occurring greenhouse gases do not. PFCs persist in the atmosphere, with lifetimes exceeding 50 000 years and have a global warming potential of at least 6500. According to the Montreal protocol, the reductions required for the stabilization of the atmospheric concentration is to stop the emission of PFCs altogether [1].

The structure of alumina has been characterised extensively due to its significance as an adsorbent and solid acid catalyst. Alumina, in particular γ-alumina (γ-Al_2O_3), contains tetragonally distorted (AlO_4) defect spinel lattices as well as the preferred, fully occupied, octahedrally coordinated (AlO_6) spinel structure. The stoichiometry of producing the appropriate ratio of Al:O in γ-Al_2O_3 cannot be accommodated by both aforementioned sublattices, which means that some spinel cation sites will be vacant and primarily exist in tetrahedral sites [2, 3]. This coordinatively unsaturated site, along with fully occupied sublattices on the surface of γ-Al_2O_3, are the sites that actively participate in catalysis.

Catalytic decomposition of PFCs has been demonstrated using an alumina-based catalyst [4, 5]. The proposed mechanism involves a 2-step hydrolysis process that takes places on the γ-Al_2O_3 surface. The rate determining step involves a bridging O atom, which connects two adjacent Al atoms that acts as the Lewis acid site to attack the PFC (e.g., CF_4) gas to form an aluminium-fluoride and aluminium-carbocation intermediate. The two intermediates then undergo a fast reaction with H_2O to form neighbouring Al-OH pairs and release CO_2 and HF as waste products. The second step is when Al-OH pairs then undergo a hydrolysis reaction to reform the Lewis acid site [4].

The focus of this research is to characterise the Lewis acid sites on the surface of γ-Al_2O_3 as a guideline to the efficiency as a catalyst decomposing PFCs. This is done using quantitative (eg. Acid-Base Titration, BET) and qualitative (eg. NEXAFS, XRD) techniques.

2. Methodology

Preparation of γ-Al_2O_3 catalyst samples: Different sample precursors were utilised as follows: Bayer gibbsite precursor samples were sourced from a commercial refinery, whilst gibbsite and pseudo-boehmite precursor samples were sourced from BASF. Precursor samples were calcined to target temperatures from 400-1000°C at 2 °C min^{-1} for 24h without quenching unless stated otherwise.

X-Ray Diffraction (XRD) for phase analysis: XRD is commonly used to analyse the phase composition of the Al_2O_3-based catalyst. The XRD pattern was obtained using a Rigaku MiniFlex™ II X-ray diffractometer with scans conducted in the 2θ range of 10-80°, with a 0.02° step size. This research looks at the different crystalline phases present in each of the calcined samples by comparing literature XRD patterns with those attained using the specified XRD.

Surface area pore analysis: Preparation of sample for analysis was done using 1g of catalyst that is dried at 110 °C for 18 hours to remove surface adsorbed gas species. Pore analyses of samples were measured using a Micromeritics Tristar 3000 instrument using nitrogen for physisorption experiments at 77 K. Specific surface areas (SSAs) were determined using the Barrett-Joyner-Halenda method [6].

Acid-Base Titration: Titration was conducted by preparing 100 mL of 0.1 mol/L of n-butylamine and placing 5 g of alumina sample and mixing for 30 minutes. The mixture is then left to sit for 5 minutes then decanted. Triplicate runs are then prepared using 25 mL of the decanted solution with methyl orange that is titrated against 0.1 mol/L solution of methanesulfonic acid until the endpoint volume is obtained.

Near-Edge X-Ray absorption fine structure (NEXAFS): NEXAFS data was obtained on the Soft X-ray (SXR) beamline at the Australian Synchrotron, the specifications and sample preparation of which have been described elsewhere [7]. Data obtained from this experiment was processed using the QANT Igor macro (Version 7.08, 2019) developed by Gann et al. [8].

3. Results and Discussion

3.1. Phase Composition Analysis

All XRD patterns shown are compared against Inorganic Crystal Structure Database (ICSD) data to identify which phases are most dominant at a specific calcination temperature. Figure 1 shows the XRD pattern of the Bayer gibbsite precursor. Calcined samples from 400 – 800 °C show a mixture of both α-Al_2O_3 and predominantly γ-Al_2O_3 phases. Upon calcination at 900 °C onwards the α-Al_2O_3 becomes the dominant phase evident by the splitting of the peak at approximately 67.8°.

Figure 2 shows that boehmite is the primary phase of the 400 °C calcined sample from lab grade gibbsite as peaks are present at approximately 14.5° and 28.2°. This is due to the partial dehydration of gibbsite around this temperature. The samples calcined at 500 – 700 °C show a γ-Al_2O_3 rich phase, whilst the sample calcined at 800 °C has κ-Al_2O_3 as the most dominant phase present, which follows the calcination pathway in literature [9].

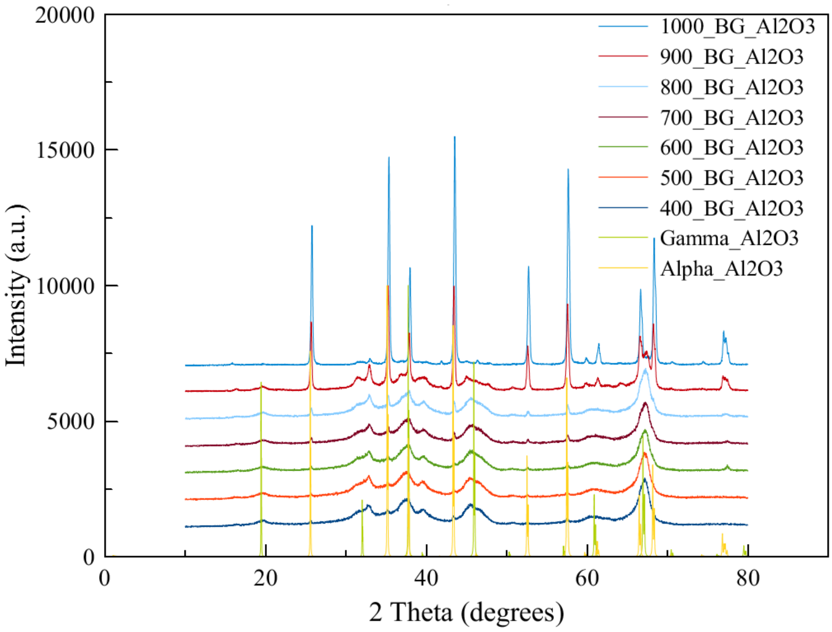

Figure 1. XRD Pattern of smelter grade alumina (SGA) from Bayer gibbsite (BG) precursor calcined from 400-1000 °C.

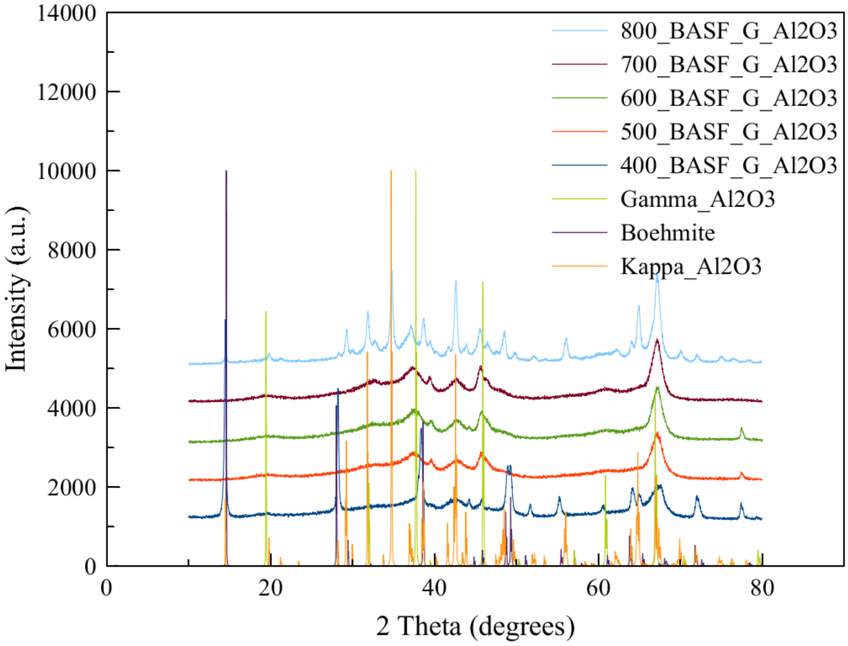

Figure 2. XRD Pattern of laboratory grade alumina (LGA) from gibbsite (BASF_G) precursor calcined from 400-800 °C.

Figure 3 shows the predominantly γ-Al_2O_3 rich phase present on all samples, using pseudo-boehmite as the precursor, calcined from 400 – 800 °C.

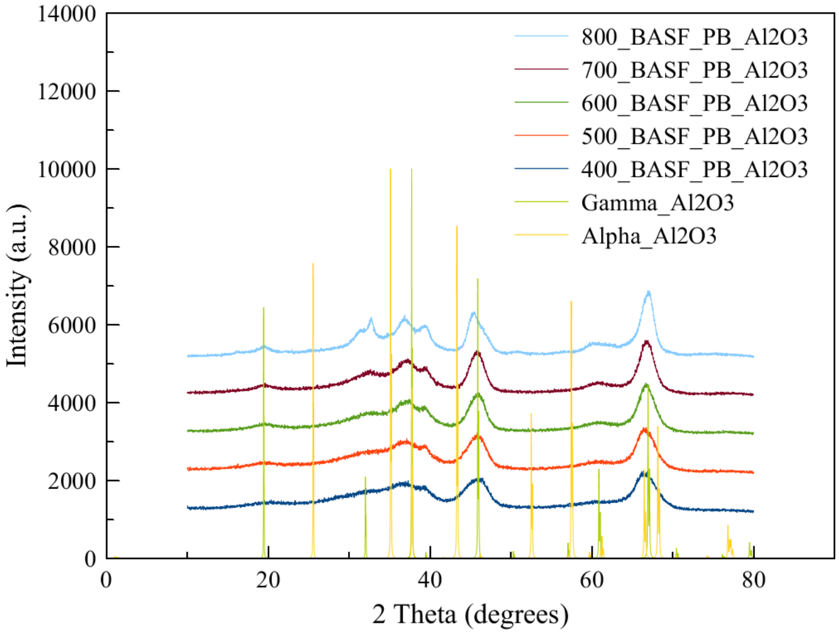

Figure 3. XRD Pattern of LGA from pseudo-boehmite (BASF_PB) precursor calcined from 400 – 800 °C.

3.2. Surface Area Pore Analysis

The analysis of the SSAs and PSD are given in Table 1. The analysis shows that samples produced from the BASF pseudo-boehmite precursor has the highest amount of surface area across all calcination temperatures, followed by the gibbsite precursor (excluding 800° due to the formation of κ-Al_2O_3), and lastly by the commercially sourced Bayer gibbsite.

Table 1. Surface area of calcined samples ranging from 400 – 1000 °C.

	BJH Adsorption Cumulative Surface Area, m²/g		
Calcination Temp. (°C)	**Typical Bayer Gibbsite**	**BASF Gibbsite**	**BASF Pseudo-Boehmite**
400	94.04	152.49	265.54
500	75.12	129.78	242.49
600	72.38	115.43	206.16
700	73.86	101.94	137.33
800	66.02	46.18	188.96
900	35.05		
1000	7.98		

3.3. Acid-Base Titration

The surface acidity, based on a *calculation by* Smith *et al*. [10] and the raw data can be seen in Figure 4. In terms of catalysis, the maximum number of Lewis acid sites per unit weight is a good indicator of performance. The ratio to surface area shown in Figure 5 is a good indicator in terms of determining an optimal catalyst on a per weight basis. The acidity of material from the commercially sourced Bayer gibbsite precursor follows a decrease from 400 °C to 500 °C, which then is followed by an upward trend to 600 °C. Between 600 – 800 °C the acidity plateaus out, which is then followed by a drastic drop to 900 °C that is likely due to the transition back into the hexagonal structure with formation of α-Al_2O_3.

The LGA sourced from gibbsite gives an approximately linear decrease as calcination temperature increases. Alumina sourced from pseudo-boehmite showed the most surface acidity compared to all samples from 400 – 800 °C. It should be noted that the surface acidity of the SGA is highest at the third lowest surface area across the sample series. This can also be seen with the 700 °C samples of both the LGA from pseudo-boehmite and the SGA sample. Both samples have drastically different surface areas but a similar surface acidity. This trend can also be observed, to a lesser extent, with the pseudo-boehmite sample at 600 °C and at 800 °C as the acidity of both samples has a surface area discrepancy > 15 m^2 and have the same surface acidity. This means that surface area alone does not dictate the acidity of a catalyst surface.

The commercial samples calcined at 700 °C and 800 °C that are presented in Figure 5 show the highest acidity per m^2 as it relates to samples that are predominantly γ-Al_2O_3. The acidity from the commercial refinery samples shows a decreasing trend from 400 – 600 °C prior to the increase in acidity at 700 °C. The number of acidic sites per unit surface area for LGA from gibbsite stagnates in between 400 and 800 °C. There is a decreasing trend from 400 – 600 °C followed by an increase to 700 °C, and a subsequent decrease to 800 °C, for the surface acidity of LGA from pseudo-boehmite.

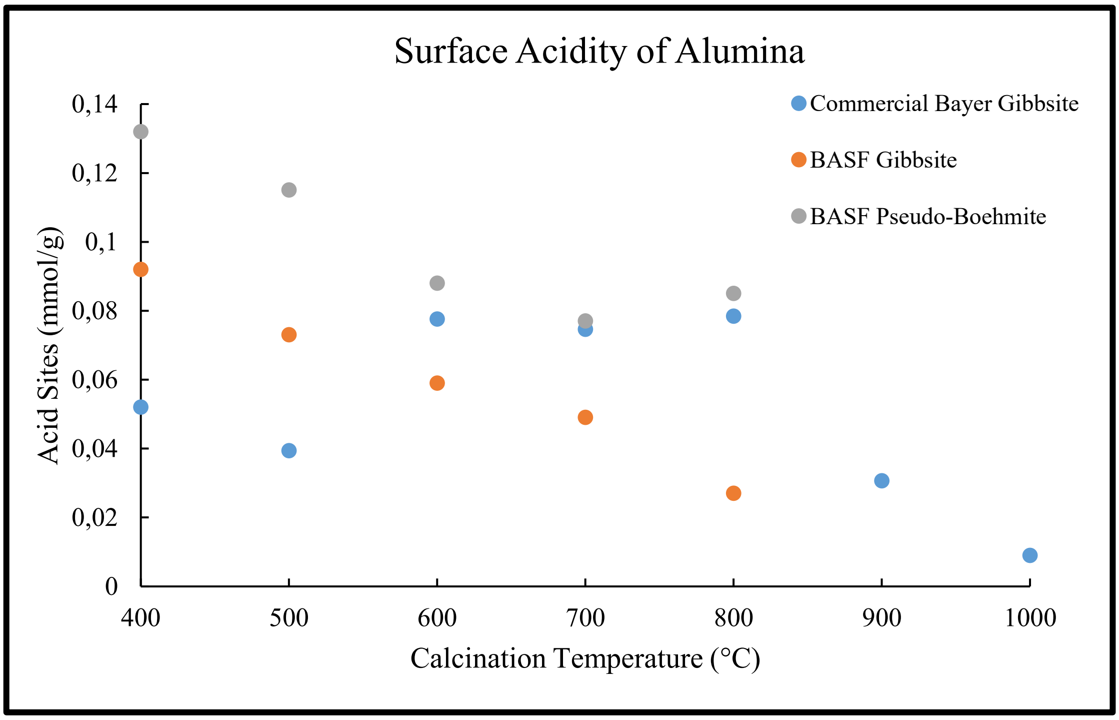

Figure 4. Surface acidity of SGA from Bayer gibbsite calcined from 400 – 1000 °C and LGA from gibbsite and pseudo-boehmite calcined from 400 – 800 °C.

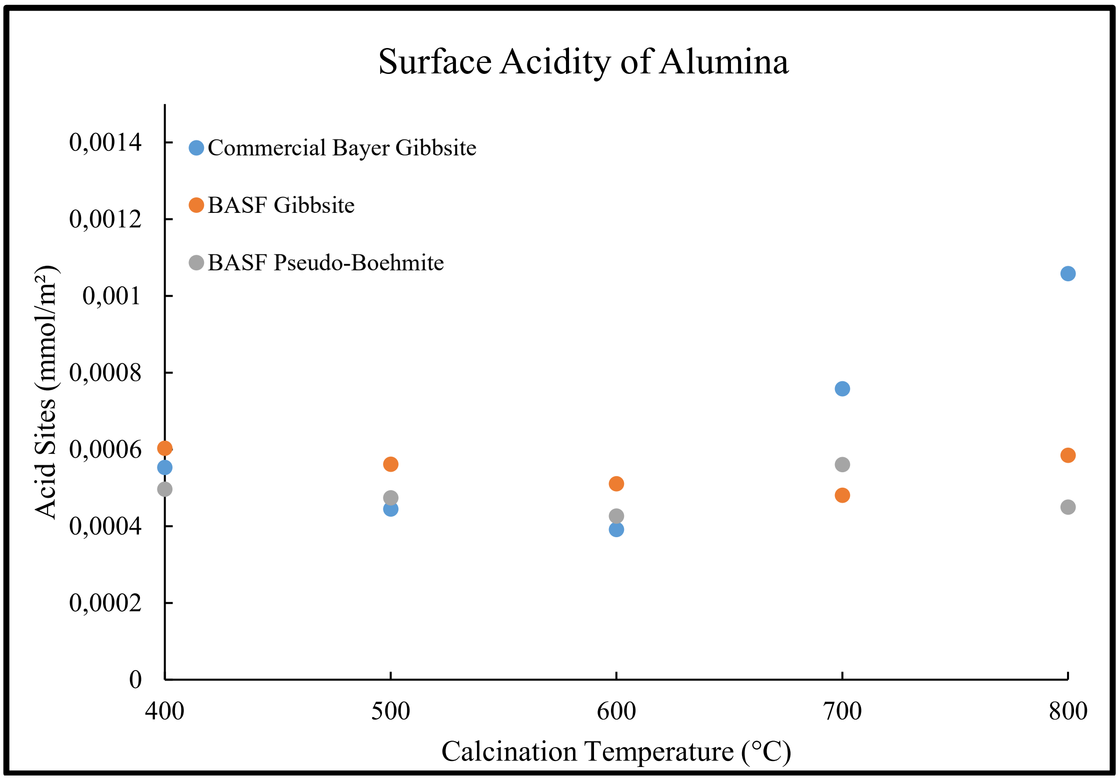

Figure 5. Surface acidity of SGA from Bayer gibbsite, and LGA from gibbsite and pseudo-boehmite calcined, from 400 – 800 °C on a per m² basis.

A distinctive difference in materials prepared using the commercial refinery-based material are the elevated sodium levels in these materials relative to those from the lab chemical precursors. The progressive segregation of soda to the surface has a significant impact on surface chemistry and we would expect on the distribution of acid sites on these surfaces.

3.4. Surface Analysis via NEXAFS

The spectra shown in Figure 6 provided more insight on the surface of the catalysts. The SGA shows three levels of the pre-edge feature at the 1566 eV region, with 400 °C and 600 °C being the most intense followed by the 800 °C sample, and the 1000 °C sample being the least intense. This feature signifies the tetrahedral coordination (AlO_4) and a higher intensity suggests more Al in this coordination are present on the sample [7]. This is a sought after feature due to higher acidity of tetrahedrally coordinated sites as opposed to octahedrally coordinated sites [11].

When comparing the different precursors in Figure 7, the pre-edge feature is most apparent from the alumina calcined from the commercial samples across all calcination temperatures which is a semiquantitative indication of having more acid sites that are tetrahedrally coordinated. Furthermore, the peaks at 1568 and 1572 eV can be assigned to the AlO_6 sites as this coordination allows the electronic transition into Al *3p* orbitals due to its symmetry [12]. The commercial sample has the more intense peaks at this energy level when compared to the laboratory sourced samples which suggests that more octahedral sites are present on the surface. This difference can be partially attributed to the surface soda present on the commercial samples as the surface chemistry is influenced by the presence of residual soda [13].

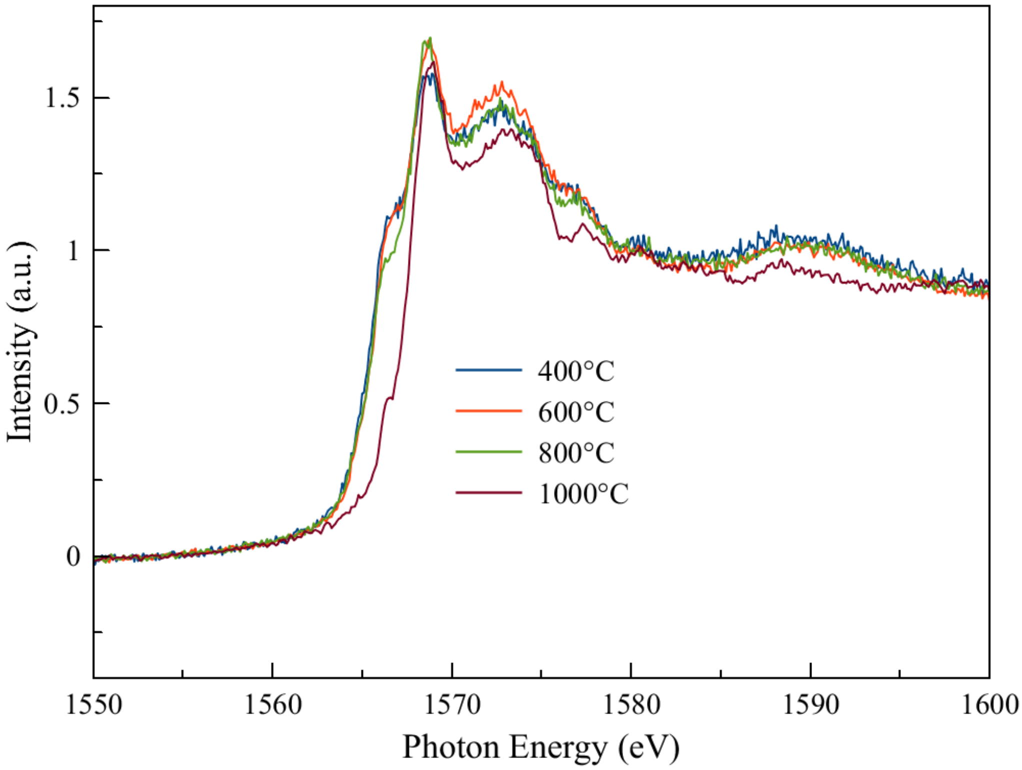

Figure 6. NEXAFS spectra of SGA from Bayer gibbsite calcined from 400 – 1000 °C.

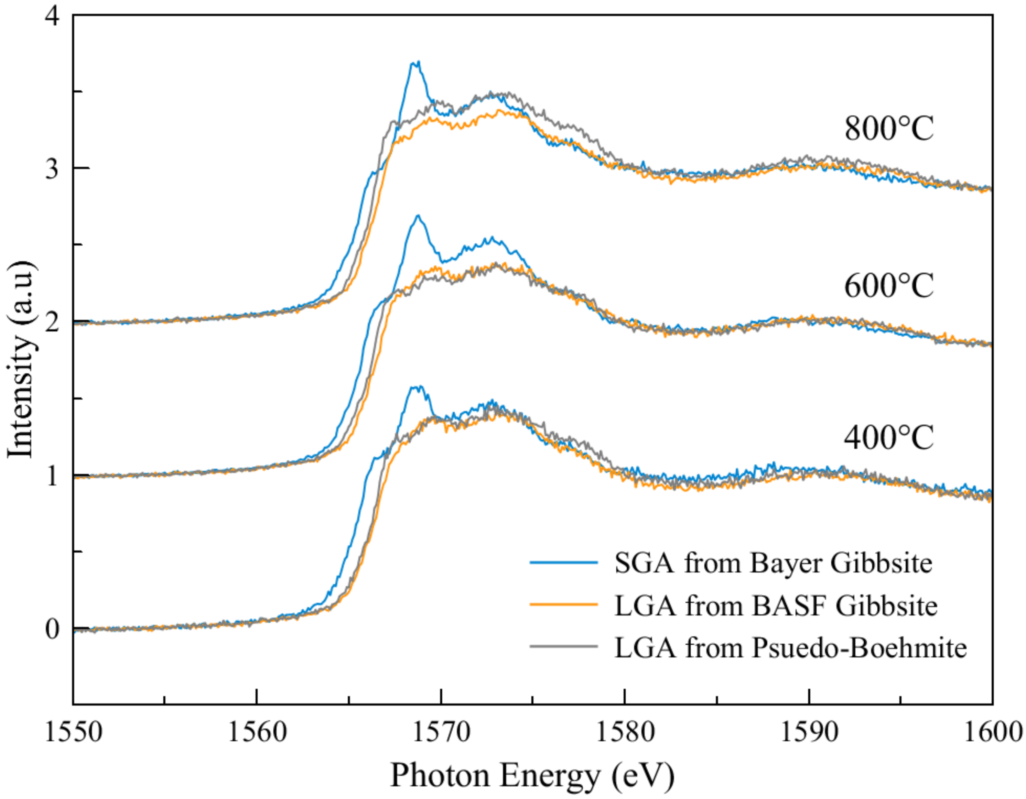

Figure 7. NEXAFS spectra of SGA calcined from commercial Bayer gibbsite, and LGA calcined from laboratory grade BASF gibbsite and pseudo-boehmite, calcined from 400 – 800 °C.

4. Conclusions and Future Work

In this study we have used a range of complementary methods to determine which Al_2O_3 based catalyst, at specified calcination temperatures, shows the highest levels of surface acidity. This gives a lead into the materials likely linked with better performance in PFC decomposition [5]. NEXAFS is a useful technique to demonstrate in which coordination acid sites are present whilst acid-base titration quantitatively shows the total acidity of the catalyst surface.

This work has provided the necessary foundations to continue screening potential catalysts that can decompose PFCs in a HF rich environment present in current industrial reduction cells. In the future, catalysts will be tested under simulated industrial environments, characterisation work to give more comprehensive data on the surface chemistry of the alumina catalyst. More complex precursors will be examined to alter the resulting surface chemistry. This will also include approaches, such as acid leaching the commercial samples to investigate the effect of soda, to provide further information on surface acidity.

5. References

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