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Heat capacity and thermodynamic functions of silica-doped γ-Al_2O_3

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ABSTRACT

Alumina can exist in a variety of structural phases, including the more common alpha and gamma phases. The gamma phase is particularly useful as a support material for catalysts, but compared to the alpha phase there is little thermodynamic data reported for it. Even less data are available for alumina prepared with dopants such as silica. These materials have improved thermal stability over their un-doped counterparts. This makes them especially useful in high temperature catalytic applications, and while they have been, in many regards, well characterized, gaps still exist in the available thermodynamic data. Additionally, water from synthesis conditions or catalytic preparation tends to bind to gamma phase alumina, further complicating thermodynamic data collection and analysis. We collected heat capacity data for a set of silica-doped alumina samples calcined at 300 °C (chemical formula Al_2O_3 0.089 SiO_2 1.190 H_2O), 600 °C (Al_2O_3 0.089 SiO_2 1.027 H_2O), 900 °C (Al_2O_3 0.089 SiO_2 0.321 H_2O), and 1100 °C (Al_2O_3 0.089 SiO_2 0.187 H_2O) using a Quantum Design Physical Properties Measurement System (PPMS). The data were fit to mathematical functions, and from these fits entropy, enthalpy, and Gibbs energy functions were calculated. The standard molar entropies for silica-doped alumina calcined at 300 °C, 600 °C, 900 °C, and 1100 °C are 101.69 $J\,K^{-1}\,mol^{-1}$, 90.206 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, 73.758 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, and 66.444 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ respectively.

1. Introduction

Alumina or aluminum oxide (Al_2O_3) is a versatile material with a wide range of applications including abrasives and abrasive protection, adhesives, paints, and sunscreen [1–3]. It is also widely used as a catalyst support [4]. This versatility arises from alumina's prevalence and the variety of structures it assumes. Alumina is known to form at least 15 distinct phases [3], including alpha, delta, theta, and gamma phases, each with distinct properties that make it appropriate for a different set of applications. Alpha alumina, for instance, is the thermodynamically stable material and, compared to other phases of alumina, quite hard [3] which makes it ideal for insular and abrasive applications. Gamma alumina is noted for its open, porous structure, which makes it an excellent material for catalysts and catalyst supports [4].

Alumina can be synthesized through a variety of methods to encourage certain characteristics. One of the simplest and most common synthetic pathways is through calcination of boehmite ($Al(OH)_3$). When calcined in air, boehmite is dehydrated and undergoes a series of complex transitions, with the gamma phase first appearing at around 250 °C, and boehmite remaining until around 500 °C. By industrial standards, a sample calcined to above 300 °C would be considered gamma phase because, while not phase pure, it has the characteristic large pores and low density of this material. When calcined in air, boehmite is dehydrated and successively transitions to gamma (300–500) °C, delta (700–800) °C, theta (900–1000) °C, and alpha phases (1000–1100) °C [4]. Although γ-alumina is stable at 500 °C, it transitions to other phases, such as α-alumina, at temperatures over 650 °C, particularly in environments with high steam concentrations. This can result in a decrease in the catalyst's efficiency, or even its deactivation [5]. Thermal instability presents a significant limitation to applications of this material.

A number of papers have been published showing the efficacy of dopants such as silica [6–12], titania [13,14], zirconia [15,16], lanthanum [17–19], and magnesium [16–20] in increasing γ-alumina's thermal stability. Mardkhe et al. developed a synthetic method for silica-doped gamma aluminas that are stable up to 1200 and even 1300 °C [5].

Thermodynamic measurements provide key insights into the properties of materials. The measurement and analysis of heat capacity, which serves as an indirect measure of energetic states [21], is particularly crucial. Because corundum, or α-alumina, has been used as a reference in calorimetric calibration [22], its heat capacity and thermodynamic properties are readily available

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[23–30]. Although some studies have explored the thermodynamic properties for other phases of alumina [31–33], data are comparatively scarce for γ-alumina, which has a very different crystal structure and is thus expected to have different thermodynamic properties [21]. The addition of a silica dopant should also have a significant impact on the heat capacity of these materials, but this data are not available in the literature.

The change in thermal stability with the addition of silica and other dopants has the potential to make significant changes to the fundamental thermodynamic properties of these materials as compared to the un-doped materials. In addition, just as absorbed water makes a significant contribution to the heat capacities of pure alumina and TiO_2 samples [34,35], the relative water content of silica-doped alumina calcined at different temperatures must be considered.

2. Experimental

2.1. Sample preparation and characterization

Materials for sample preparation were purchased from Alfa Aesar and used without further purification. Silica-doped alumina samples were prepared according to a patented method developed by Mardkhe et al. [5]. A 1:5 M ratio of aluminum isopropoxide (AIP) to water was mixed with 5 wt% silica from tetraethylorthosilicate (TEOS) and a 1:2 mol ratio of TEOS to water in the absence of a template for 30 min using a Bosch mixer. This precursor material was placed in a sealed plastic jar at room temperature and aged overnight, then calcined by heating in a muffle furnace in air with a ramp rate of 2.33 $°C{\cdot}min^{-1}$ and held at a predetermined temperature for two hours. The final calcination temperature leads to different pore properties and to different amounts of water physisorbed and chemisorbed to the sample surface. In this paper, samples will be referred to by their final calcination temperature; for instance, the sample heated to 300° C will be referred to as SDA 300, where SDA stands for silica-doped alumina.

Following synthesis, the samples were characterized using a variety of techniques to obtain information about their purity, structure, phase, pore properties, and water content. X-ray diffraction data collected in a 2θ range of 10°–80° was used to identify the alumina phase, and was performed using a Panalytical X'Pert Pro X-ray diffractometer operating with a fixed power source (40 mV and 40 mA) at a spinning rate of $0.02°{\cdot}s^{-1}$. The results are shown in Fig. 1 along with peak information for a γ-alumina standard. A strict assignment to the phase gamma alumina cannot necessarily be made for the sample calcined to a lower temperature, as these are expected to be mixtures of boehmite and gamma phases. A Micromeritics Tristar 3020 operating at −196 °C was used for nitrogen adsorption measurements, and the resulting data analyzed using the Slit Pore Geometry model described in a previous publication [36]. Chemical purity and relative content was determined by ICP-OES. Results of the BET characterization are summarized in Table 1, and further details are available in earlier publications [5].

Although the water content had previously been measured for these materials, heat capacity measurements led us to be interested in more tightly bound chemisorbed water, as opposed to the outermost layers of physisorbed water. To remove loosely bound water, each sample was dried in a muffle furnace at 150 °C for 24 h, and samples were stored and handled in an argon atmosphere between drying and measurement to limit re-adsorption of atmospheric water. The water content was determined by thermogravimetric analysis (TGA) carried out using a Netzsch STA 409PC instrument. Approximately 20 mg samples were loaded into a platinum sample pan and heated from 25 °C to 900 °C under 20 $mL{\cdot}min^{-1}$ of He gas flow with a heating rate of 3 $°C{\cdot}min^{-1}$. The mass of each sample was constant by the end of the measurement, indicating complete desorption of water from the sample surface. Graphs of sample mass as a function of temperature for each sample are included in Fig. 2. Water content calculated from these measurements is included in Table 1.

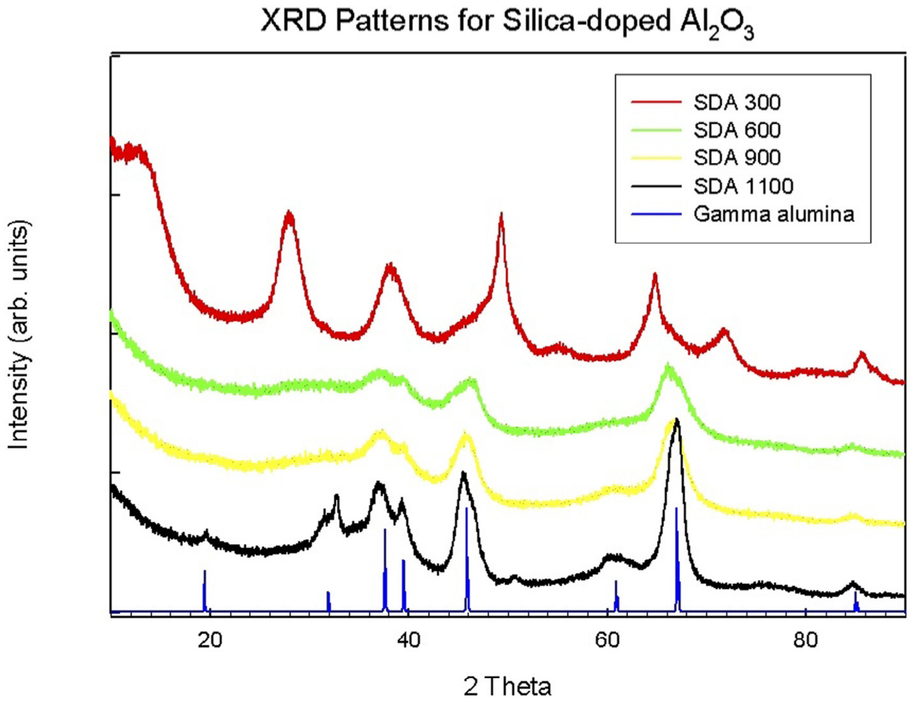

Fig. 1. XRD patterns of all alumina samples.