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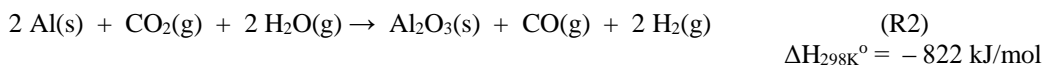
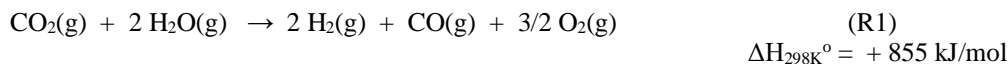
Project Title: Investigation of Liquid-Alloy Based Growth of Alumina Aerogels

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RESEARCH PROGRESS REPORT – 9/1/2018 to 8/31/2019

Summary: Continued investigations of the activation of aluminum, both pure and in alloys, have been pursued using a liquid Galinstan alloy (66.5% (wt. %) Ga, 20.5% In and 13.0% Sn) under flowing gas streams of wet and dry CO₂. In these reactions the aluminum metal has been found to reduce CO₂ and H₂O to mixtures of CO and H₂, i.e., syngas, depending on the conditions. The reaction is spontaneous at near room temperature and works with both aluminum-based alloys and pure aluminum. In a new research direction, the activated aluminum was also investigated for the growth of high-surface-area aluminum nitride by reactions with melamine as the ammonia source during its thermal decomposition. Aluminum nitride was discovered to form at low temperatures, and as well, yielded the simultaneous formation of a high-surface-area carbon nitride phase. The structures and properties of the carbon-nitride compound has been characterized by X-ray diffraction, UV-Vis and IR spectroscopy, and found to have a layered structure that can provide coordination to monovalent and divalent metal cations.

Research Description: The activation of aluminium metal has been investigated by its dissolution into a liquid Galinstan, and which we have shown can lead to the reduction of CO₂ and H₂O to syngas, i.e., CO and H₂. A patent has been filled for intellectual protection of this discovery. Chemical thermodynamics shows that the reaction of CO₂ and H₂O (R1; below) is highly unfavored to occur at room temperature, accompanied by a relatively small entropy term and temperature dependence. However, the use of activated aluminium as a powerful reductant (and elimination of O₂(g) as a product in R1), yields a highly energetically-favourable reaction (R2; below) that can proceed at room temperature within the liquid Galinstan alloy.



Preliminary data has provided confirmation that reaction R2 can occur near room temperature, as verified by detection of CO and H₂ during the concomitant growth of the alumina aerogel. The reaction of CO₂ alone proceeds at relatively slower rates, yielding CO, Al₂O₃, and a minor amount of unidentified aluminum oxycarbides. Conditions to produce an ideal syngas mixture of 2:1 for H₂:CO are under investigation.

Reactions of the activated aluminium with a source of ammonia, e.g., via the thermal decomposition of melamine, were also investigated to target the formation of a high-surface-area aluminium nitride. In the initial reaction, the formation of aluminium nitride was observed together with the formation of what was subsequently characterized to be an amorphous carbon nitride compound. Subsequent synthetic attempts using a LiCl/KCl flux mixture were able to produce a crystalline and layered form of the carbon nitride compound as characterized by powder

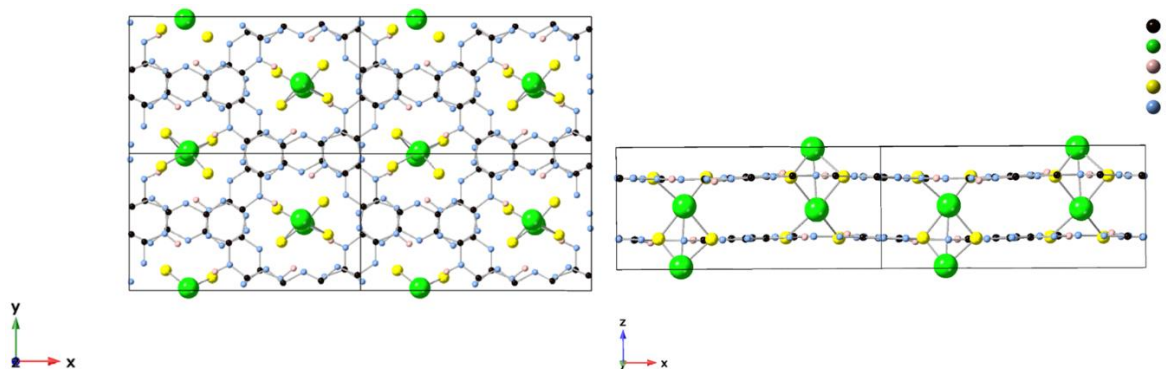


Figure 1. View of the layered crystalline structure of PTI $[(\text{C}_3\text{N}_3)_2(\text{NH}_x\text{Li}_{x-1})_3\text{LiCl}]$ oriented down the z-axis (left) and the y-axis (right). Color coding of the atom types are provided by the legend.

X-ray diffraction. The structure of the compound as determined using Rietveld refinement techniques, shown in Figure 1, was found to have the chemical formula of $[(C_3N_3)_2(NH_xLi_{x-1})_3LiCl]$ (i.e., polytriazine imide) and form in an orthorhombic unit cell ($P2_12_12_1$) with dimensions of $a = 14.5580 \text{ \AA}$, $b = 8.6030 \text{ \AA}$, and $c = 6.7502 \text{ \AA}$. Typically, the formation of this compound occurs with the release of the ammonia within the sealed fused-silica reaction vessel, and frequently causing the vessel to rupture.

Motivated by recent studies of high-surface-area PTI that have shown a number of potentially interesting properties as catalysts and as filters, intense synthetic studies were undertaken to attempt to grow larger single crystal samples for property measurements. Crystalline growth of the carbon-nitride PTI phase was investigated as a function of reaction temperature (i.e., 450, 470, 500, and 600 °C), the salt to melamine ratio (i.e., 1:1, 5:1, 11:1, 15:1, 20:1, and 45:1 molar ratios), as well as the heating rate (i.e., 8 °C per hour and 4 °C per min) and cooling rate (i.e., quenching,

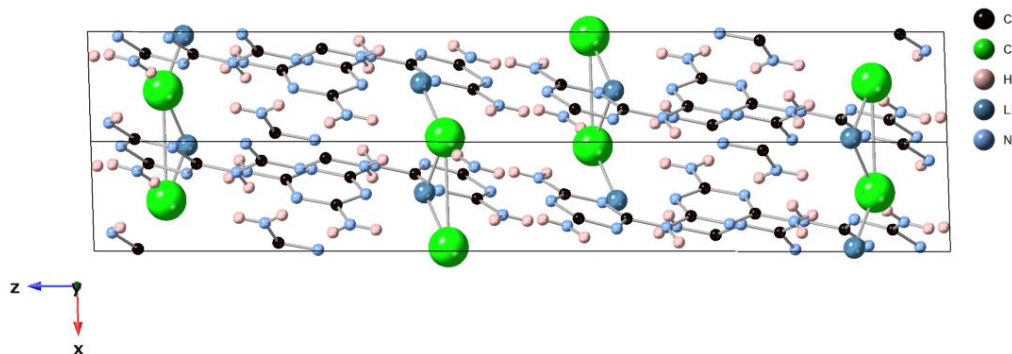


Figure 2. View of the crystalline structure of melam-LiCl $[(C_6N_{11}H_9)LiCl]$ oriented down the y-axis. Color coding of the atom types are provided by the legend.

2 °C per hour, and 1 °C per hour) and the reaction times (i.e., 12hr, 24hr, 36hr, 48hr, and 72hr). It was discovered that by starting with melamine, a polycrystalline carbon nitride material could be created in one step within a short reaction time (470 °C at

a 5:1 molar ratio, and within ~12 hr). While large crystals of PTI have yet to be prepared, new crystals of a melam-LiCl grew as clear rods with sizes in the micrometer range. The crystals were characterized by single crystal X-ray diffraction to have the structure as illustrated in Figure 2. The new melam-LiCl crystals were found to form when either salt loading was near 1:1 or reaction temperatures were as low as ~450 °C.

The flux-mediated exchange of Li^+ cations for transition metal cations (e.g., Ag^+ , Cu^{2+} , Mn^{2+}) was also explored as a path to the chemical and electronic functionalization of the carbon nitride compounds, such as starting from the PTI compound. The PTI crystalline structure contains pores within its layers that can accommodate cations at up to six different crystallographic sites. The exchange of Li^+ cations was investigated using several approaches, including hydrothermal reactions with $CuCl_2$, a eutectic mixture of dry $CuCl_2$ and KCl , and a triaxial mixture of anhydrous $LiCl$, KCl , and anhydrous $CuCl_2$. Recent results show that up to 100% of the Li^+ cations can be exchanged, with higher amounts of transition-metal cations resulting in two new carbon nitride compounds that have not yet been fully characterized or published. Preliminary results show that a range of monovalent and divalent transition-metal cations can be accommodated into the PTI structure. These are currently being characterized using powder X-ray diffraction, BET surface areas, FT-IR, UV-Vis spectroscopy, electron microscopy, and magnetic susceptibility measurements. The underlying structure of the carbon-nitride structure is maintained, but with growing amounts of the transition metal cations seemingly yielding large changes in the stacking arrangements between the carbon nitride layers. A scientific paper on their comprehensive structural characterization and physical property measurements are planned upon completion of these investigations.

Impact of the Research: These research efforts have yielded a number of novel and very interesting directions, including the growth of alumina aerogel materials with the concomitant production of an H_2 and CO syngas mixture, as well as the formation of new carbon nitride compounds. A new patent application was filed and a federal proposal was prepared that focuses on recycling aluminum and on the growth of aerogel materials. Current and prior results and funding have significantly strengthened my future proposals. One undergraduate (co-inventor) and two graduate students involved on this project have received training in powder X-ray diffraction techniques, including both data collection and subsequent data analysis, as well as training in physical property measurements on solid-state materials. The undergraduate student was motivated to pursue summer research and is currently applying for graduate programs in chemistry and materials science departments. One of the graduate students will be attending a Gordon Research Conference next year to present the results of the above research efforts.