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METAL CATALYSED INTUMESCENCE: Characterisation of the Thermal Decomposition of Calcium Gluconate Monohydrate

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ABSTRACT

Calcium gluconate monohydrate is a member of a new class of base-catalysed intumescent compounds. It forms low-density closed-cell carbonaceous foam when exposed to heat. The volume expansion can be as high as two hundred times the original volume. At temperatures above 750°C this foam is transformed into a porous, yet cohesive, structure based on calcium oxide. The latter has only a slightly higher density and shows significant flame-resistance.

KEY WORDS: X-ray diffraction, infrared spectroscopy, scanning electron microscopy, thermal analysis, pyrolysis, intumescent, carbon, foam, closed-cell.

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1.   Introduction

Intumescent fire retardant additives form a foamed protective layer when exposed to heat [1]. They are widely used in coatings while applications in solid polymers are still being established [2]. Classic intumescent systems are based on the acid catalysed dehydration of polyalcohols [2,3]. It has been known for some time that the presence of certain metals in cellulose increases the carbon residue formed during pyrolysis [4]. Recently, we reported intumescence catalysed by organometallic complexes, including potassium tartrate [5]. Shortcomings of these systems include the open-cell structure of the foams produced as well as their impermanence owing to the metal-catalysed solid-state oxidation of the residual carbon. Since then we have discovered a new class of compounds that produce voluminous closed cell foams [6]. Here we report on the foaming properties of a prime example, calcium gluconate monohydrate.

2.   Experimental

Approximately 1 g samples of calcium gluconate monohydrate were placed inside glass Polytop^{TM} bottles measuring 23,5 mm ϕ by 100 mm. The samples were pyrolysed in a laboratory furnace using both air and inert (N_2) atmospheres. Temperatures between 200°C and 1000°C in 50°C or 100°C intervals were investigated. Each sample was placed in the preheated furnace for 5 minutes. After removal from the furnace, the samples were allowed to cool in desiccators. The mass loss was determined gravimetrically and the density estimated from the foam heights.

The foams were characterised as follows: X-Ray Diffraction (XRD) analysis was performed on a Siemens D-501 automated diffractometer. Infrared spectroscopy (IR) spectra were

obtained from a Brooker IFS 113 spectrometer at low pressures (operated at 32 scans, 2 cm^{-1} resolution, powder samples in pressed KBr pellets). Low magnification Scanning Electron Microscopy (SEM) images of gold-coated samples were obtained on a JEOL 840 SEM. Uncoated samples were viewed with a JEOL JSM 6000F cold field emission gun scanning electron microscope at high magnifications. A Netsch STA 409 simultaneous DSC/TGA instrument was used for the thermal and gravimetric analysis. The analyses were done in either air or argon atmospheres at a scan rate of 10 °C/min.

3.   Results and Discussion

When exposed to the high heat of an open gas flame, calcium gluconate monohydrate shows profuse foam generation. Initially the foam is black but on continued flame exposure it shrinks slightly and turns white. The white foam is very stable to high heat. It glows with an orange luminosity when held in the gas flame.

Figure 1 shows the temperature-dependant mass loss and apparent density of foams obtained by oven-pyrolysis in an air atmosphere. Mass loss commences above 100°C and the sample mass reaches a residual plateau value of 12,5% at 1000°C consistent with the complete conversion of the monohydrate to calcium oxide. Density decreases from the initial ca. 560 kg/m^3 bulk density of calcium gluconate monohydrate to a minimum value of ca. 2,5 kg/m^3 for the sample pyrolysed at a temperature of 300°C. Beyond this temperature gradual densification of the foam occurs reaching a value of ca. 20 kg/m^3 at 1000°C. This change in density is accompanied by a simultaneous and gradual change in colour of the cooled foam from brown to black then grey and ultimately to white. XRD shows that the white residue obtained at 1000°C consists primarily of calcium oxide.

The foam structure for inert and air pyrolysed samples were similar. The SEM pictures (Figure 2) show that the carbonaceous foam generated at intermediate temperatures has a closed-cell structure with very thin cell walls. At 400°C the cells were between 50 μm and 200 μm in size. The cell wall thickness was estimated from other SEM photographs and varied from 5 nm to 50 nm. At pyrolysis temperatures above 500°C the foam structure changed to open-cell.

SEM also revealed that the white residue obtained at 1000°C has an open-cell structure. This implies that the high temperature pyrolysis of calcium gluconate can produce an inorganic oxide of low bulk density and high specific surface area.

The following phases were identified in the powder diffraction patterns of the pyrolysis residues: the precursor compound in its hydrated and anhydrous forms, calcium carbonate, calcium oxide and calcium hydroxide. The presence of calcium hydroxide is attributed to the reaction of the high-surface area oxide with atmospheric moisture during handling and sample preparation subsequent to pyrolysis. All the XRD spectra, irrespective of the atmosphere used, also showed an amorphous halo indicating the presence of amorphous carbon. The halo was less pronounced in the samples pyrolysed in an air atmosphere owing to the loss of carbon through oxidation. This conclusion is supported by the fact that pyrolysis in air resulted in a higher mass loss than pyrolysis in the inert atmosphere.

For the samples pyrolysed in air the results of the XRD spectra indicate the following sequence of events: The dehydration of the mono-hydrate commences at ca. 150°C and is

essentially complete at 200°C. Calcium carbonate formation starts at 300°C and it is converted to the oxide above 750°C. Essentially the same sequence of events is observed for the samples pyrolysed in a nitrogen atmosphere except that the onset of $CaCO_3$ formation is delayed until about 700°C.

The thermal analysis results are reported in Figure 3 (air atmosphere) and Figure 4 (argon atmosphere). The loss of crystal water above 120°C is indicated by the initial mass loss of 4 %. This mass loss is associated with an endothermic peak at 140-150°C. The second endothermic peak at 180-210°C probably corresponds with the release of water through dehydration reactions. The overall mass loss in argon of about 42% is only slightly below the expected 44% for removing all the hydroxyl groups as water and the 54% if in addition, one CO_2 is released as well. In the inert atmosphere there is another broad endothermic peak centred at ca 550°C. However, in the air atmosphere there is a sharp exotherm in the DSC signal and a corresponding sudden mass loss in the TGA at ca. 570°C. This corresponds to the catalytic oxidation of the residual carbon by the calcium oxide as observed previously for other base catalysed systems [5]. This phenomenon is responsible for the afterglow effect in polymers flame retarded with inorganic compounds [7]. This air-oxidation provides the explanation for the comparatively higher residual mass obtained in an inert atmosphere: more carbon is retained, as it is not oxidised. The mass loss above ca. 650°C for both samples is attributed to the conversion of $CaCO_3$ into CaO.

Figure 5 shows the evolution of the IR spectrum as the pyrolysis temperature is increased. Comparing the samples pyrolysed at similar temperatures indicates slower decomposition in the inert atmosphere. Alcohol groups and hydrogen-carbon bonds were retained to higher

heating temperatures in the absence of oxygen, while $CaCO_3$, CaO and $Ca(OH)_2$ all formed at lower temperatures in the presence of air.

At temperatures below 150°C, the spectrum is similar to that of the pure material. Above 200°C, the peaks associated with free (3500 cm^{-1}) and bound (3200 cm^{-1}) –OH groups decrease in intensity indicating a progressive loss in alcohol groups. The absorption peak at ca. 1450 cm^{-1} indicates the formation of carbon-carbon double bonds. This peak can be identified at temperatures as low as 200°C in nitrogen and at 250°C in air. It grows stronger with increasing temperature and then wanes again above 700°C. The onset for the decomposition to calcium carbonate ($CaCO_3$) occurs at about 300°C in air. A sharp peak at 800cm^{-1} is well established at 700°C and is characteristic for calcium carbonate. By 800°C it has virtually disappeared. Simultaneously a sharp peak at 3650 appears that is indicative of the presence of $Ca(OH)_2$. The latter formed when the CaO pyrolysis residue reacted with atmospheric moisture.

4.   Conclusion

Calcium gluconate monohydrate shows a substantial volume expansion when pyrolysed at high temperatures. On the basis of pyrolysis, thermal analysis, XRD and IR evidence we conclude that this foaming action is caused by water vaporisation that is derived from loosely bound water of crystallisation as well as the dehydration of the many hydroxyl groups on the molecule. Most of the expansion occurs in the narrow temperature range of 120-250°C. The primary product of decomposition is amorphous carbon that is retained in the absence of oxygen up to a temperature of 700°C. In the presence of air $CaCO_3$ is formed at temperatures as low as 300°C and the residual carbon is rapidly oxidised at 550-650°C. In the absence of

air, $CaCO_3$ is only formed above 700°C. In both instances the $CaCO_3$ is converted into CaO above 750°C.

The main differences in the behaviour in an inert and an air atmosphere are that the rate of decomposition in air is faster, less amorphous carbon is formed and the carbon is lost at a lower temperature. The density of the intumescent foam reaches a minimum of ca. 2.5 kg/m^3 at a pyrolysis temperature of 300°C. The SEM images showed that the pyrolysis product, obtained at temperatures below 500°C in air, is a homogeneous thin-walled, closed-cell foam. At higher pyrolysis temperatures the foam loses the closed-celled structure as it is converted into a monolithic porous calcium oxide residue. The low bulk densities of the product obtained at respectively 700°C or 1000°C also implies that a calcium carbonate or a calcium oxide with a high specific surface area can be prepared in this manner.

5.   Acknowledgments

6.   References

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