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STUDIES OF LAYERED AND CHANNEL COMPLEXES USING COMBINED THERMOGRAVIMETRY AND MASS SPECTROMETRY

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Abstract

The rate of removal and uptake of guests into layered and porous materials is important in many areas of materials chemistry. Here we report on the use of atmospheric thermogravimetry linked to a mass spectrometer (TG-MS) to investigate the thermal characteristics of three different solids. We show that (i) the desorption of cyclohexylamine from the surface of a pillared acid activated smectite clay occurs in two stages, indicating two possible acidic binding sites, (ii) TG-MS is an extremely sensitive technique for probing progressive anion exchange of lithium aluminium layered double hydroxides, (iii) on heating, the perhydrate $4Na_2SO_4{\cdot}NH_4Cl{\cdot}2H_2O_2$ releases H_2O_2 intact.

Keywords: layered double hydroxide, perhydrate, pillared acid activated,TG–MS,

Introduction

Thermogravimetry (TG) is well established as a powerful tool in materials chemistry. In many cases the various mass loss steps can be assigned to particular species either by the expected mass loss or by the sequence of their release. However, TG curves can often be complicated, but interpretation may be enhanced by combined use of TG and mass spectrometry (MS), enabling specific species to be detected at given temperatures of release. This is termed evolved gas analysis (EGA). A review by Dollimore *et al.* [1] and more recent articles by Redfern [2] have set out the ideal requirements of any combined system. EGA can be achieved by use of a TG-MS in which the thermobalance is at a comparable pressure and in close proximity to the MS analyser. Alternatively the two apparatuses can be physically linked with a transfer line and a molecular leak. Here we report the results obtained by implementing the latter approach, which involved modifying our existing thermobalance and linking it to a mass spectrometer.

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Three types of compounds were examined.

1. Clay minerals consist of 2D silicate sheets which are separated by small hydrated interlayer cations. In the smectite clay group, the distance between the sheets can be increased by the intercalation of large polyhydroxymetal cations, through ion exchange [3]. This results in an expanded, porous material [4]. Upon heating, the polycations are converted to stable metal oxides which act as pillars and permanently prop the clay sheets apart. The resulting 'pillared clay' is usually microporous, thermally stable and possesses increased surface area and surface acidity compared to the non pillared clay. These materials, therefore, have a wide range of applications such as acid catalysts and adsorbents [4]. If the host clay is treated with acid at high temperature (acid activation) prior to the intercalation of the pillars, a pillared material of intrinsically greater acidity, surface area and pore volume can be produced [5].

The Brönsted acidity of a clay is defined as its proton-donating ability [6]. The extent of acid activation and hence the quality of the clay as a catalyst, can be measured by sorption of cyclohexylamine [7]. It is assumed that when cyclohexylamine is adsorbed, each molecule of cyclohexylamine associates with one proton acid site [7]. Thus the number of protons available and accessible to the cyclohexylamine may be calculated from the weight of bound cyclohexylamine desorbed. We were interested in whether any adsorbed cyclohexylamine is released outside the 350–400°C temperature range normally associated with its desorption.

2. Layered double hydroxides (LDHs) are mixed metal hydroxides with the general formula $[M^{Z+}_{1-x}M^{3+}_{x}(OH)_2]^{A+}X^{m-}_{A/m}\cdot nH_2O$, where A=x for z=2 and A=2x for z=1 [8]. This formula is usually abbreviated to $M^{z+}M^{3+}X^{m-}$. The structure consists of a cationic layered framework separated by charge balancing interlayer anions and water. The water is hydrogen bonded to the framework hydroxides. These 'anionic clays' have many uses such as catalysts, catalyst supports, ion exchangers and adsorbents [9]. However, unlike smectite clays, LDHs are not thermally stable: when heated, the interlayer species are liberated, followed by collapse of the layers and decomposition into the amorphous mixed metal oxides.

A variety of lithium aluminium LDHs may be synthesised from a carbonate-containing precursor by exchange of the interlayer anions [10]. Here, the synthesis of $LiAlNO_3$ from $LiAlCO_3$ is investigated by comparison of the TG-MS traces obtained for samples after different periods of exchange of carbonate for nitrate.

3. Perhydrates are compounds which contain hydrogen peroxide of crystallisation and are important in bleach formulations for powder detergents. Much work has focused on sodium carbonate perhydrate [11] and the oxalate perhydrates [12]. However, little has been published on the properties of the isostructural inclusion compounds $4Na_2SO_4\cdot MCl\cdot 2H_2O_2$ (M=Na [13], K [14] and NH_4 [15]). The H_2O_2 are contained within channels defined by a host lattice of $4Na_2SO_4\cdot MCl$. The sodium salt has shown interesting behaviour in that once the

H_2O_2 is thermally desorbed, it can be readily reintroduced into the solid [16]. This family of perhydrates generally has outstanding thermal stability in comparison with other perhydrates, loss of hydrogen peroxide occurring only after about 150°C. We were interested to ascertain whether the H_2O_2 is liberated intact or whether decomposition into H_2O and O_2 within the crystal occurs first.

Experimental

Apparatus

The housing of a Polymer Laboratories TGA 1500 was modified to contain a ceramic pipe, situated directly above the thermobalance crucible. This enabled any gases released during heating of the sample to pass along a fine heated quartz capillary tube into, and slightly beyond, a T-piece pumped by a rotary pump. The third exit of the T-piece lead to a Leda Mass Mini-Lab quadrupole MS chamber via a molecular leak. The mass spectrometer had a mass range of 0–300 amu and the choice between use of Faraday cup or Secondary Electron Multiplier. The pressure inside the T-piece could be adjusted by use of a Negretti valve. The thermobalance remained at atmospheric pressure under N_2 (25 ml min^{-1}) whilst the pressure within the MS chamber was typically 8×10^{-4} Pa. The time lead (i.e. the transfer time between gas evolution and detection) was less than 1 s. The design, shown in Fig. 1, enabled simultaneous TG-MS data to be collected.

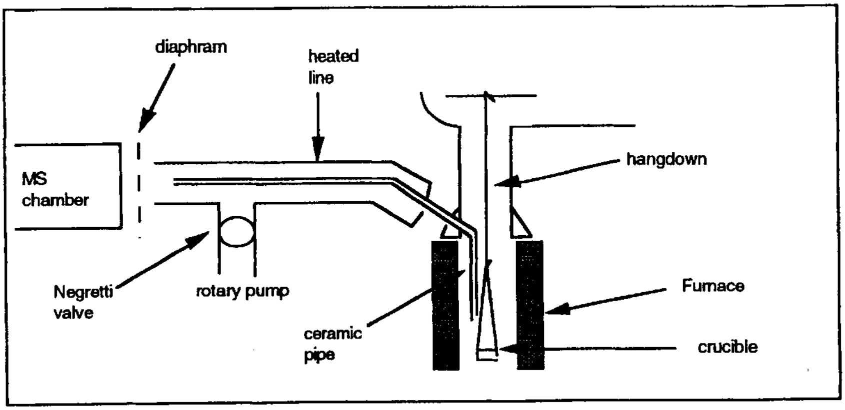

Fig. 1 Design of the link between the TG apparatus and the MS

Syntheses

Pillared acid activated montmorillonite clay

Details of acid activation and pillaring are published elsewhere [17]. The clay was exposed to liquid cyclohexylamine at room temperature for ca. 16 h and then heated at 80°C for 3 h in order to remove any physisorbed amine. Mass loss corresponding to desorption of cyclohexylamine is expected between 350–400°C so the thermobalance was heated to 500°C at a heating rate of 10°C min^{-1}.

LDHs

The synthesis of $LiAlCO_3$ is described elsewhere [10] and conversion to $LiAlNO_3$ was carried out as follows: $LiAlCO_3$ (1.0 g) was added to 150 ml distilled, deionised water and the *pH* adjusted to 4.5 by addition of 0.1 mol l^{-1} HNO_3. The addition was accompanied by expulsion of CO_2. The mixture was stirred whilst maintaining the *pH* at 4.5 by further addition of acid. The resulting product was isolated by filtration or centrifugation and washed thoroughly with hot distilled water until no nitrate could be detected in the supernatant liquor. In this way four samples were studied: $LiAlCO_3$ and $LiAlCO_3$ exchanged for 24, 48 and 72 h. TG was performed at a heating rate of 30°C min^{-1}.

$4Na_2SO_4 \cdot NH_4Cl \cdot 2H_2O_2$

A solution of 0.77 g NH_4Cl in 16 g 30% H_2O_2 was added dropwise to a solution of 8.18 g of Na_2SO_4 in 40 g 30% H_2O_2. The resulting solution was left to crystallise in air to yield well formed crystals. These were then ground (which was shown not to affect the H_2O_2 content). TG data were collected using a heating rate of 10°C min^{-1}.

Results and discussion

Pillared acid activated montmorillonite clay

Figures 2a and b show the DTG and TG curves respectively of the clay following cyclohexylamine adsorption. The TG curve shows a continuous mass loss but three transitions are resolved by the DTG curve. The two species expected to be released during thermal treatment are H_2O and cyclohexylamine. The MS trace for $m/z=18$ (Fig. 2c) shows that H_2O is continuously released up to 300°C. Most H_2O is lost below 100°C as indicated by the first DTG peak and the sharp MS peak. This is loosely bound physisorbed H_2O. Strongly bound interlayer H_2O is released between 100–300°C (Fig. 2c) and contributes to the middle DTG peak (120–250°C).

The molecular weight of cyclohexylamine is 99 but the fragment, C_4H_8 (m/z 56), was found to give a clearer MS trace. Figure 2d shows two forms of cyclohexylamine to be present, both stable beyond 150°C. That there is no peak below this temperature suggests all physisorbed cyclohexylamine has been removed by heating at 80°C. Since the temperature of desorption is related to how tightly the Brönsted sites bind to the cyclohexylamine, this result indicates that there is more than one type of acid site available to the cyclohexylamine. Most

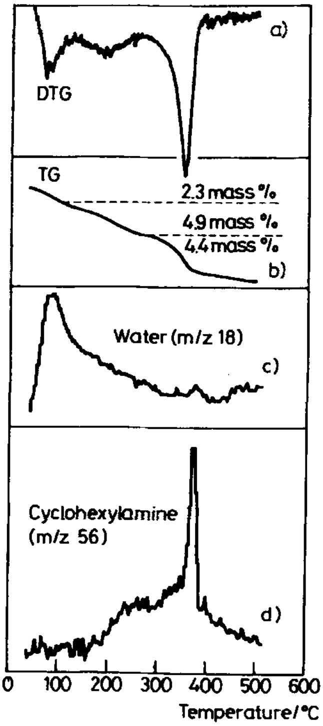

Fig. 2 DTG (a) , TG (b), MS *m/z* 18, and (d) MS *m/z* 56 for desorption of cyclohexyl-amine from the surface of a pillared acid activated smectite clay (c)

cyclohexylamine is strongly adsorbed and gives rise to sharp DTG and MS peaks (370°C). It is the quantity of this strongly bound cyclohexylamine which is used for determining the acidity of a clay. More weakly bound cyclohexylamine gives a broad peak (200–350°C) in the MS which also contributes to the middle DTG peak centred at 190°C. It is clear that without MS analysis, given the overlap with the loss of water, it is possible to assign wrongly mass loss in the region to water evolution. Detection of this more weakly bound cyclohexylamine is in agreement with DTG results obtained by Ballantine *et al.* [18].

$LiAlCO_3$ and $LiAlNO_3$ layered double hydroxides (LDH's)

When these LDHs are heated, the liberated interlayer anions decompose to yield CO_2 and NO_2 respectively. These gases are best detected in the mass spectrometer using NO (*m/z* 30) and CO_2 (*m/z* 44). Figure 3 shows the progressive formation of $LiAlNO_3$ from $LiAlCO_3$ as evidenced by DTG. The trace obtained after 72 h exchange corresponds to $LiAlNO_3$. In the literature, the mass losses are normally assigned, without MS, according to related materials and by the sequence of evolution. Thus the first mass loss below 200 °C is the liberation of physisorbed and interlamellar water. This water loss (1) results in broad peaks for the first three traces in Fig. 3 but in a very clear peak in $LiAlNO_3$. The second transition (2) is dehydroxylation of the layers. Note that there is a shift in dehydroxylation to higher temperatures in the nitrate (300°C) in comparison to the carbonate (250°C). This trend is further thought to be indicated in the liberation of the anion, a reproducible complex peak corresponding to carbonate at about 275°C (3) and a comparatively simple peak due to nitrate at 550°C (4).

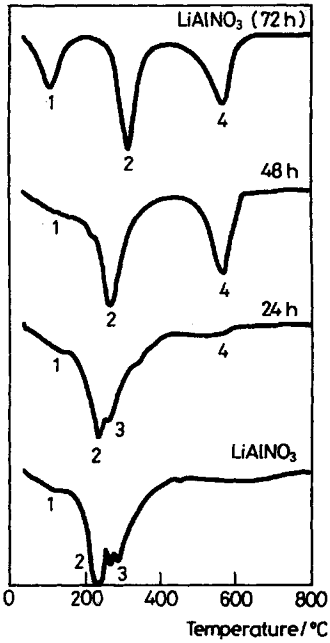

Fig. 3 DTG of $LiAlCO_3$ and nitrate-exchanged $LiAlCO_3$ for 24, 48 and 72 h

That such assignments are correct is confirmed here for the first time for such materials by the use of mass spectroscopy. Figure 4 shows the same progression observed by the linked mass spectrometer using (a) CO_2 (*m/z* 44), (b) NO (*m/z* 30). As the exchange proceeds, the peaks (1, 2, 3) due to *m/z* 44 are lost and peaks appear for *m/z* 30 (4, 5, 6). Due to differences in the sample masses used, a systematic decrease/increase is not observed. Note that in the MS trace of $LiAlCO_3$ the complex DTG curve is resolved into two peaks due to carbonate indicating two sources of CO_2 unstable below 500°C. A further source at 700°C, (3), very broad and hardly discernible in the DTG curve, is also observed in the MS trace and probably corresponds to some carbonate impurity. The main CO_2 peak at about 330°C (2) corresponds to interlayer carbonate and, on exchange, there is a slight shift in temperature of release as the layers are destabilised. The shoulder on this peak (1) is due to a less stable form of carbonate. That this form is stable to 24 h exchange, shows that it is not a carbonate impurity.

After 24 h there are 3 discernible peaks corresponding to *m/z* 30. The first peak (4) is present in each of the exchanged samples at about 390°C whilst the intermediate peak at 500°C (5) is only observed at 24 h. The main peak at 590°C (6) is characteristic interlayer nitrate. There are several possible explanations for the occurrence of three NO peaks. The first is that exchange proceeds giving layers of nitrate and layers of carbonate rather than layers containing a mixture of the anions. This is in agreement with the work of Weber *et al.* [19]. If this is the case, nitrate layers adjacent to other nitrate layers will have different binding energies to those adjacent to a carbonate layer, thus giving rise to a different temperature of decomposition. This will be reflected in the MS of carbonate and several types of carbonate are evident in Fig. 4.

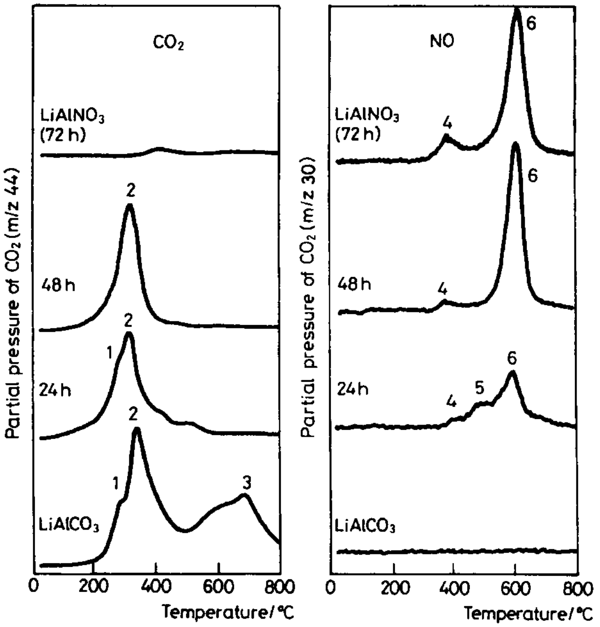

Fig. 4 Evolution of (a) CO_2 (*m/z* 30) and (b) NO_2 (*m/z* 30) from $LiAlCO_3$ and nitrate-exchanged $LiAlCO_3$ for 24, 48 and 72 h

The second possible explanation for more than one type of anion is that the anion is regarded as being associated with either the interlayer region or with lithium or aluminium cations. This would give rise to three types of anion as seen in the NO trace after 24 h, in Fig. 4.

Sodium sulphate ammonium chloride perhydrate *($4Na_2SO_4{\cdot}NH_4Cl{\cdot}2H_2O_2$) [ISSACP]*

Figure 5 shows the traces obtained by TG-MS, scanning *m/z* 15 (NH), *m/z* 18 (H_2O), *m/z* 32 (O_2), *m/z* 34 (H_2O_2) and *m/z* 44 (CO_2). There are three mass losses observed in the TG curve of SSACP. The first, at 60°C, is shown to be 1% by weight of physisorbed H_2O by the MS peak at *m/z* 18. The second mass loss of 10%, between 150 and 200°C, corresponds to the loss of $2H_2O_2$ per formula unit. That a peak is observed for *m/z* 34, shows that some H_2O_2 is being released intact. The presence of peaks at *m/z* 18 and *m/z* 32 do not themselves unambiguously confirm that H_2O_2 is released intact since these would also result from (i) the H_2O_2 decomposing en route to the mass spectrometer or (ii) the H_2O_2 being released as H_2O and O_2.

The onset of the third mass loss overlaps the final stages of H_2O_2 release and corresponds to a weight loss of 7.4% i.e. sublimation of NH_4Cl. The broad NH peak (using *m/z* 15) in the MS trace mirrors the assignment in the TG curve.

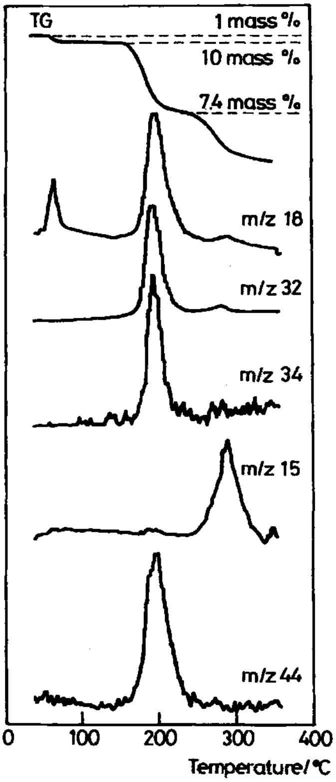

Fig. 5 TG and MS evidence for H_2O_2 (*m/z* 34) and CO_2 (*m/z* 44) evolution from SSACP

Figure 5 also suggests that CO_2 (*m/z* 44) is being released coincidentally with H_2O_2. Since the release appears sharp and occurs at the same temperature as that of H_2O_2, it is unlikely to be an instrument artifact. The use of analytically pure reagents in the synthesis suggests it unlikely that there are carbonate impurities in the sample. A more reasonable explanation is that atmospheric CO_2 has been absorbed into the structure during synthesis of crystallisation. In either case, the concentrations are very low and is a good example of the sensitivity of the technique.

Concluding remarks

Relatively simple modifications to an existing thermobalance has enabled more detailed information to be obtained concerning the thermal properties of a variety of compounds. In the first example, we have proved that mass losses in the 350–400°C temperature range correspond to desorption of cyclohexylamine adsorbed on a pillared acid activated smectite clay. However, cyclohexylamine is also desorbed between 200–350°C, indicating more than one type of acid site. In the same way, more than one type of binding for the anion has been shown to be present in partially and fully nitrate-exchanged $LiAlCO_3$. The perhydrate $4Na_2SO_4 \cdot NH_4Cl \cdot 2H_2O_2$ releases H_2O_2 intact. We have also shown that there is also reproducible evidence that CO_2 is adsorbed within the lattice.

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