

## APPLICATION OF EVOLVED GAS ANALYSIS TO SURFACE CHARACTERIZATION OF ORGANICALLY-MODIFIED INORGANIC MATERIALS

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### ABSTRACT

Evolved gas analysis has been used in the routine characterization of organically-modified oxides, silicates and phosphates. Titania and kieselguhr, both modified with a bis-amino silane, show similar characteristics. In each case, surface hydrogencarbonates yield CO<sub>2</sub> and H<sub>2</sub>O, before the organic species dissociate in two steps. During modification with a mono-amino silane the surface of a borosilicate glass retains three organic layers, two of which are probably hydrogen-bonded. After treating with  $\beta$ -phenylalanine the structure of zirconium phosphate is comprised of pillared layers. During programmed heating the pillars collapse and reactions can occur between the gaseous products, leading to the evolution of a mixture of aromatic compounds.

### INTRODUCTION

Porous inorganic compounds (such as oxides, silicates and phosphates) can act as stable substrates to which organic molecules can be bonded. The resultant materials may then be active in specific, and often diverse, types of reactions. For example, silicas modified by amino-silanes have been used to extract metal ions [1] and to separate enantiomers [2]; some have also been found to exhibit anti-microbial activity [3].

Although a variety of experimental techniques [4] have been used to study modified inorganic materials, there is clearly a need for a single simple method of routine characterization. Even when available, many modern

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techniques of surface science do not fall within this category because they require special treatment of the sample or the use of a simpler analogue of the real surface. Traditional forms of thermal analysis (e.g. thermogravimetry or differential thermal analysis) are much more widely available, and are particularly suited to studies of polycrystalline samples, but on their own do not provide enough unambiguous information. However, evolved gas analysis (EGA) is a technique which can straddle both surface chemistry and thermal analysis, and which may allow the nature of a surface to be deduced through monitoring of the gaseous species released during programmed heating.

In characterizing organically-modified inorganic materials by EGA we have used equipment designed originally for catalytic studies [5]. An important feature of the apparatus (compared to some commercially available systems) is that an inert carrier-gas passes *through* a bed of sample and sweeps the evolved species to the detector, so ensuring rapid analysis and limiting the extent of readsorption on the sample surface.

## EXPERIMENTAL

### *Materials*

We added organo-silanes to three inorganic compounds which had substantially different surface areas. Titanium(IV) oxide in the form of rutile (British Titan Products; measured surface area =  $14 \text{ m}^2 \text{ g}^{-1}$ ) and kieselguhr (Fluka Chemicals; nominal surface area =  $100 \text{ m}^2 \text{ g}^{-1}$ ) were modified by addition of 3-(2-aminoethylamino)propyltrimethoxysilane (Fluka Chemicals). Amorphous silicate glass (British Nuclear Fuels plc; measured surface area =  $3.2 \text{ m}^2 \text{ g}^{-1}$ ) was reacted with 3-aminopropyltriethoxysilane (Lancaster Synthesis).

Each inorganic sample (10 g) was dried by heating under reflux with toluene (methylbenzene); the water was collected in a Dean and Stark volatile component trap. The silane ( $10 \text{ cm}^3$ ) was then added, and the mixture heated under reflux for a further 4 h. During heating, the methoxy/ethoxy portions of the modifying groups were eliminated as alcohol, which collected in the trap. The modified material was isolated by filtration and washed with acetone (propanone) and toluene, before being gently heated (at ca. 320 K) under vacuum (for 3 h) to remove the solvents. Finally, the solid was sieved and the 60- to 150- mesh powder retained for testing.

To assess the usefulness of EGA as a technique for characterizing a variety of modified inorganic solids, we also tested a layered material, which had been prepared by the direct addition of aqueous  $\beta$ -phenylalanine ( $\beta$ -2-amino-3-phenylpropanoic acid) to zirconium(IV) phosphate [6].

### Evolved gas analysis

A short bed (ca. 1 cm) of material (200 mg) was loaded (between two small plugs of glass wool) into a glass-lined stainless steel reactor (SGE Ltd.), which was then positioned inside a horizontal tube-furnace. A thermocouple (NiCr–NiAl) attached to the reactor detected the temperature in the immediate vicinity of the sample bed. The heating rate and maximum temperature were set using a temperature programmer (Eurotherm, Type 818).

High purity helium (BOC Ltd.) was the inert carrier-gas used to transfer evolved or desorbed gas-phase species from the sample to the point of detection. Before reaching the reactor, the helium was passed through activated copper to remove any oxygen, and through a cold trap at 77 K to remove traces of water and carbon dioxide. A constant flow rate ( $30 \text{ cm}^3 \text{ min}^{-1}$  at 101325 Pa) was maintained through the sample by setting a flow controller (Negretti and Zambra Ltd.), which was fitted in the gas supply line prior to the cold trap. A splitting valve (SGE, Type MCV/100) linked the reactor to a vacuum chamber, which was pumped turbomolecularly and contained the detector from a quadrupole mass spectrometer (Spectramass, Type Dataquad 100-V3.15). Depending on the setting of the splitting valve, either all the gas could be vented through a bubble flow-meter, or a portion could be sampled. The valve and the vacuum chamber were enclosed by a thermostatic box (at 375 K) to avoid condensation.

During EGA the sample was heated at  $10 \text{ K min}^{-1}$  to 775 K, while specific peaks in the mass spectrum (Table 1) were repeatedly scanned and their partial pressures recorded as a function of temperature. Although not all the mass/charge ratios were unambiguous (e.g. peaks  $m/e = 28$  and 44 could be due either to the organic species or to other carbon-containing adsorbates), the coincident occurrence of peak maxima did often allow the nature of surface species to be deduced. To confirm that the selected peaks were representative of all the evolved species, a fresh sample of a modified

TABLE 1  
Mass spectral peaks monitored during EGA

Functional group	Selected peaks
3-(2-aminoethylamino)propyl- $-(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$	$m/e = 15$ ( $\text{>NH}$ ), 28 ( $-\text{C}_2\text{H}_4-$ ), 42 ( $-\text{C}_3\text{H}_6-$ ), 44 ( $-\text{C}_2\text{H}_4\text{NH}_2$ ), 57 ( $-\text{C}_3\text{H}_6\text{NH}-$ )
3-aminopropyl- $-(\text{CH}_2)_3\text{NH}_2$	$m/e = 15$ ( $\text{>NH}$ ), 28 ( $-\text{C}_2\text{H}_4-$ ), 42 ( $-\text{C}_3\text{H}_6-$ ), 57 ( $-\text{C}_3\text{H}_6\text{NH}-$ )
$\beta$ -phenylalanine $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$	$m/e = 14$ ( $-\text{CH}_2$ ), 15 ( $\text{>NH}$ ), 44 ( $-\text{COO}-$ ), 78 ( $\text{C}_6\text{H}_6$ )

material could be heated very slowly and the complete mass spectrum recorded at selected temperatures.

In order to check that there were no further changes beyond the range of EGA, separate thermogravimetric experiments (up to 1000 K) were carried out using a microbalance (Sartorius, Type 4433 MP8-1), which was heated by a vertical tube-furnace.

## RESULTS AND DISCUSSION

### *TiO<sub>2</sub> modified with 3-(2-aminoethylamino)propyltrimethoxysilane*

The EGA trace for modified TiO<sub>2</sub> (Fig. 1) showed maxima for three of the selected peaks coinciding between 350 and 400 K. From the relative intensities, two of the peaks ( $m/e = 28$ , 44) can be attributed to CO<sub>2</sub> ( $I_{28} : I_{44} = 6.6 : 100$ ). The simultaneous desorption of H<sub>2</sub>O and CO<sub>2</sub> implies the presence of hydrogencarbonates (or similar species with the same stoichiometry) on the surface of the amphoteric TiO<sub>2</sub> (eqn. (1)). These

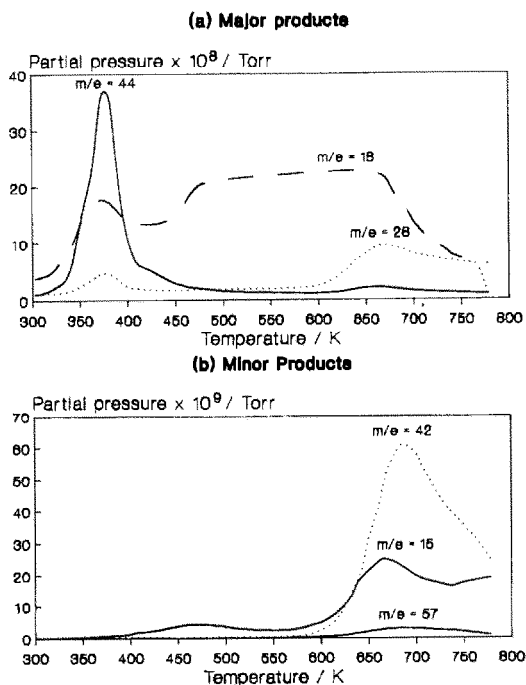
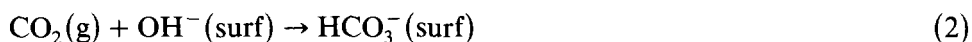
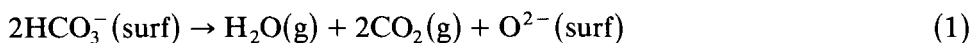


Fig. 1. EGA of titanium(IV) oxide modified with 3-(2-aminoethylamino)propyltrimethoxysilane: (a) major products; (b) minor products. 1 Torr = 101325/760 Pa.

species can arise from the adsorption of  $\text{CO}_2$  at basic hydroxyl sites (eqn. (2)) [7]



EGA of the substrate showed very little desorption of  $\text{CO}_2$ , indicating that the hydrogencarbonate species were formed during, or as a result of, modification. Furthermore, the broad maximum for  $\text{H}_2\text{O}$ , between 450 and 750 K (Fig. 1a), provided evidence of the modified surface being extensively hydroxylated. We consider, therefore, that the  $\text{HCO}_3^-$  and many of the  $\text{OH}^-$  species were created by some of the methoxy groups (from the organo-silane) dissociating and combining with surface oxide ions on the  $\text{TiO}_2$  during the preparation of the modified material.

Decomposition of the organic species began at ca. 580 K, with the process clearly occurring in two consecutive steps. Maxima for one set of peaks ( $m/e = 15, 28, 44$ ) corresponding to fragments of  $-\text{C}_2\text{H}_4\text{NH}_2$  were closely followed by maxima for peaks ( $m/e = 42, 57$ ) associated with the remaining portion,  $-\text{C}_3\text{H}_6\text{NH}-$ . Thus, it appears that fission of the central C–N bond preceded the breaking of the bond between the terminal carbon atom and the silicon, which anchored the bis-amino species to the substrate [1].

The intensity of the  $m/e = 15$  peak increased slightly above its background level between 400 and 550 K (Fig. 1b), but there was no coincident increase in the other organic peaks being monitored. In order to determine the cause of this small maximum, another sample of the modified material was heated to 485 K and the complete mass spectrum was monitored. Several peaks ( $m/e = 29, 31, 32, 91, 92$ ) increased noticeably in intensity and, as well as the peak at  $m/e = 15$ , several others ( $m/e = 39, 51, 65$ ) increased slightly. These peaks indicated that some methanol ( $m/e = 15, 29, 31, 32$ ) and toluene ( $m/e = 39, 51, 65, 91, 92$ ) had been strongly retained by the surface during modification.

#### *Kieselguhr modified with 3-(2-aminoethylamino)propyltrimethoxysilane*

EGA of untreated kieselguhr showed the desorption of water, leading to a large clearly defined maximum at 410 K and a smaller but broader maximum centred at 730 K (Fig. 2). This behaviour is typical of the dehydration of silica [8]. The first step is due to the loss of  $\text{H}_2\text{O}$  molecules, which are hydrogen-bonded to surface silanols; more water is evolved during the desorption of specific hydroxyl groups, resulting in the formation of oxygen bridges between adjacent silicon atoms [8].

There are definite similarities between the EGA traces for the modified samples of kieselguhr (Fig. 3) and  $\text{TiO}_2$  (Fig. 1), reflecting similar surface compositions and essentially the same stages of decomposition for both

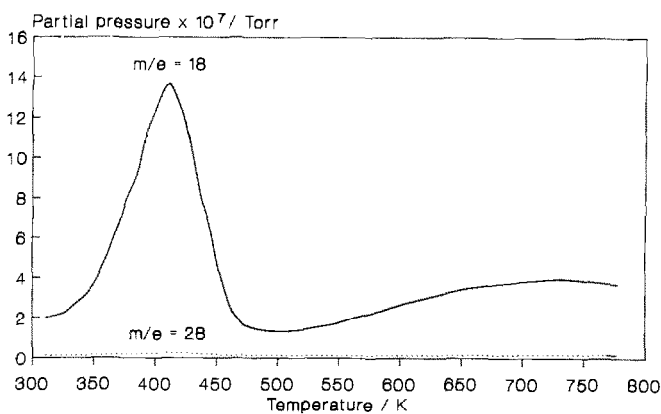


Fig. 2. EGA of kieselguhr.

materials. However, in the case of the kieselguhr, the maxima occurred at higher temperatures, indicating either higher activation energies for the dissociation of the surface species or considerable re-adsorption within the pores. Furthermore, the small maxima ( $m/e = 15, 42$ ) at ca. 560 K suggest a second layer, which was not extensive and which was weakly bound. This layer could have been comprised of bis-amino species which were

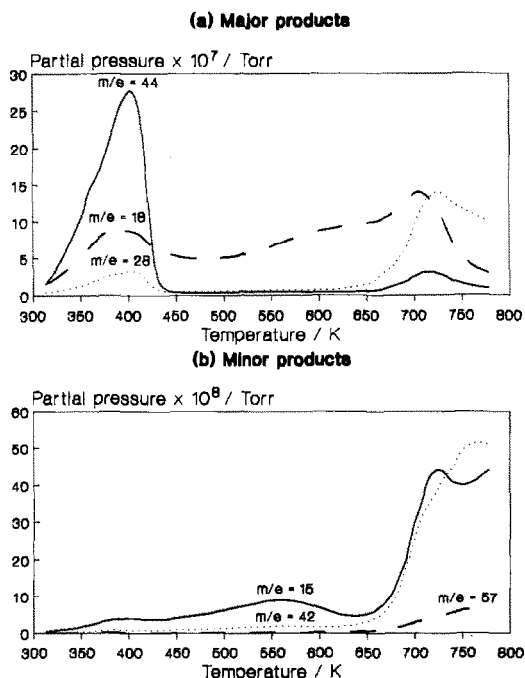


Fig. 3. EGA of kieselguhr modified with 3-(2-aminoethylamino)propyltrimethoxysilane: (a) major products; (b) minor products.

hydrogen-bonded either to the first layer or to silanol groups at the surface, but the exact nature of the bonding cannot be resolved from EGA alone. The formation of the second layer seems to have been limited (probably by steric factors) to the extreme surface, i.e. it did not occur within the pores.

As the formation of  $\text{HCO}_3^-$  on pure silica is not a facile process [9], the appearance of such species on our modified samples implicates the impurities known to be present in kieselguhr. Typically, these are mainly aluminium and iron at levels of 0.1–1.0% by mass, and smaller amounts of alkali and alkaline-earth metals [10]. Even at low concentrations, however, segregation can occur; for example, only a very small proportion of Fe ( $< 0.1\%$  by mass) forms a solid solution in  $\text{SiO}_2$ , the rest tending to crystallize as  $\text{Fe}_2\text{O}_3$  on the surface [11]. Our experiments suggest, therefore, that the silica surface was greatly enriched by amphoteric and basic metal oxides, which were largely responsible for the creation of hydrogencarbonates during the elimination of the methoxy groups of the organo-silane.

#### *Borosilicate modified with 3-aminopropyltriethoxysilane*

The EGA trace for modified borosilicate (Fig. 4) contained maxima for peaks associated with the amine at ca. 420 and ca. 770 K. Furthermore, the

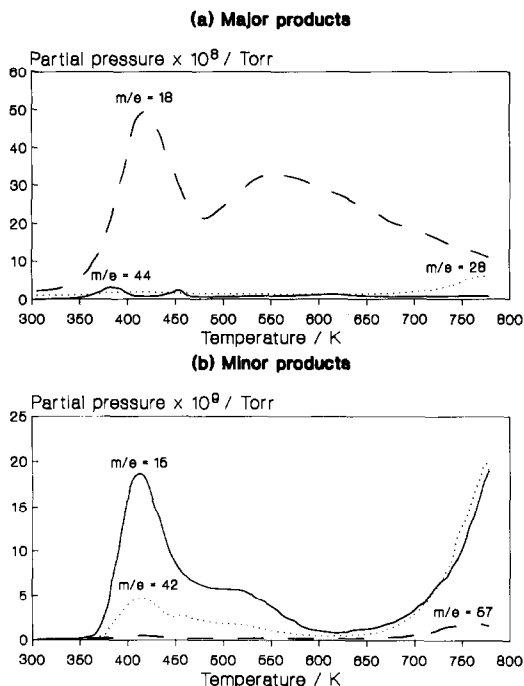


Fig. 4. EGA of borosilicate modified with aminopropyltriethoxysilane: (a) major products; (b) minor products.

maxima had definite shoulders on their high temperature side (450–500 K). Collectively, these features suggest that there are three types of the organic species present at the surface. The desorption of the most weakly held of these was accompanied by the evolution of water, implying that surface hydroxyl groups provided the sites to which the adsorbate was hydrogen-bonded. It seems likely that the other weakly bound species, which gave rise to the shoulders on the maxima, were also hydrogen-bonded, probably as a second layer partially covering the most stable (covalently bound) organic species.

The presence of separate small maxima for peak  $m/e = 44$  (Fig. 4(a)) indicates that there were also some surface carbonates or carboxyl species present on the modified glass.

#### *Zirconium(IV) phosphate modified with $\beta$ -phenylalanine*

Dissociation of the phenylalanine occurred in two consecutive steps, which closely followed the coincident desorption of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Fig. 5). The relative positions of the peak maxima indicate that, during the destruction of the organic layer, dissociation of the carboxyl groups (into  $\text{CO}$ ,  $\text{CO}_2$

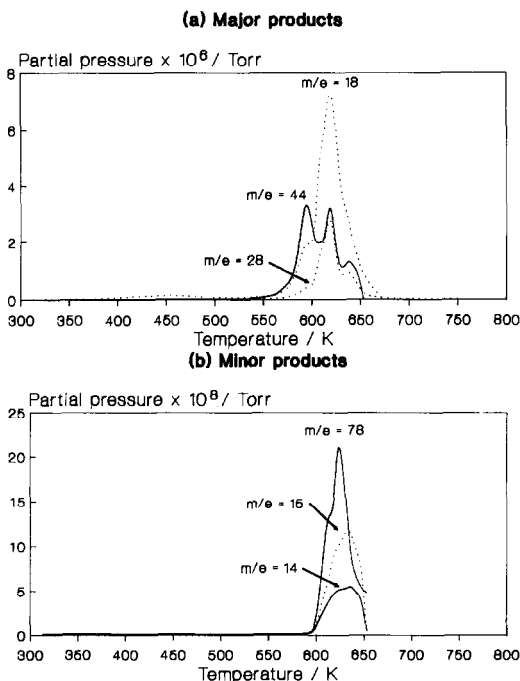


Fig. 5. EGA of zirconium(IV) phosphate modified with  $\beta$ -phenylalanine: (a) major products; (b) minor products.



and H<sub>2</sub>O) and elimination of benzene preceded the decomposition of the alanine.

In a separate study [6], it was observed that the difference between the interlayer spacing in zirconium phosphate modified by  $\beta$ -alanine and that in a sample treated with  $\beta$ -phenylalanine was equivalent to the diameter of a benzene ring. It was concluded that the organic species have a pillaring effect. During EGA, the organic pillars 'collapsed' in two successive stages. Furthermore, reaction of the evolved products seemed to occur within the cavities, leading to the formation of a viscous aromatic product which blocked the capillary tubing (linking the reactor to the vacuum chamber) and brought the experiment to an end at ca. 650 K.

## CONCLUSIONS

Although EGA is a well established technique [12,13], which has been applied to surface studies of catalysts [5,14], it has largely been overlooked as a method for characterizing inorganic materials which have been deliberately modified. However, by using EGA and adopting the approach of a surface chemist, a material scientist can hope to derive information about the following.

- (i) The range of thermal stability of a modified surface (by using different carrier-gases, the effect of atmosphere can also be studied).
- (ii) The nature of surface species other than those deliberately added (such adsorbates may block or interfere with addition of the required phase).
- (iii) The number of organic layers formed during modification, or the number of different types of sites at which adsorption can occur.
- (iv) Whether the modifying species are held strongly (covalently) or weakly (hydrogen-bonded) on the substrate.

At present, one of the main disadvantages of using EGA in the study of modified materials is that its predictive power is limited by a lack of related data. Its potential can be appreciated by comparison with catalytic studies, in which the extensive use of temperature-programmed methods (correlated with other techniques of surface analysis) has meant that the active sites in some catalytic systems can now be accurately deduced from a simple desorption experiment [5,15]. An important application of EGA may be as a means of inducing and monitoring reactions at the surfaces of or in the spaces between layers of a substrate.

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