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Applications of new high resolution evolved-gas analysis systems for the characterisation of catalysts using rate-controlled thermal analysis[☆]

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Abstract

The advantages of using rate-controlled thermal analysis (RCTA) methods in the thermal characterisation of catalysts are described. The use of these methods is demonstrated by the temperature programmed reduction of vanadium pentoxide, the measurement of the number and type of acid sites in clays by temperature programmed desorption of cyclohexylamine, and temperature programmed reaction, which is illustrated by the dehydration of propan-2-ol over an acid-activated montmorillonite clay. It is shown that the new system has advantages in the study of the kinetics of reactions and in improving resolution when used to characterise the thermal decomposition of catalyst precursors.

New evolved-gas analysis systems for characterising heterogeneous catalysts are described, in which a variety of RCTA methods is used. The systems are computer-controlled and use a variety of furnaces, permitting samples from a few microgrammes to fifty milligrammes to be studied, under pressures ranging from ultra high vacuum to one atmosphere. The furnace chosen for a particular experiment is linked to one of a number of gas detectors (hygrometers, katharometers and mass spectrometers), the output of which completes the control loop. The most important component of the system is the versatile software which supports a range of RCTA modes, including conventional linear heating rate, constant reaction rate, and other control strategies developed in this work.

Keywords: Acid sites; Catalysts; Clophill clay; Dolomite; Montmorillonite clay; Rate controlled thermal analysis (RCTA); Temperature programmed desorption; Temperature programmed reaction; Temperature programmed reduction; Vanadium pentoxide reduction

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1. Introduction

Thermal analysis (TA) techniques are widely used in many fields of study. Conventionally, linear heating rates are used in which significant temperature and pressure gradients can be created in the sample. The magnitude of these gradients is influenced by many factors. Some of these are instrumental and include the design of furnace and the diameter of thermcouple wires, etc. Others are operational, for example, the heating rate, the thermal conductivity and flow rate of purge gas. Parameters relating to the sample also play a part and include its heat capacity, thermal conductivity, mass, particle size, degree of compaction and the enthalpy change of the process being studied. The greater the heating rate, the higher the temperature and pressure gradients across the sample, giving apparently elevated peak temperatures and poor resolution of adjacent events. Furthermore, the reaction rate varies considerably during the course of such experiments, even when the heating rate is zero, as in isothermal work. For reactions involving reversible processes, e.g. the decomposition of many catalytically important precursor materials such as hydroxides and carbonates, the varying pressure of product gas throughout the process can exert a marked influence on the rate of the process and so affects the results of characterisation experiments and the properties of the resulting product.

The judicious use of heating regimes which are modified, in some manner, by the reaction rate can greatly reduce the problems outlined above, giving enhanced resolution in analytical and characterisation techniques. For example, Rouquerol [1] developed controlled transformation rate TA, now commonly known as constant rate TA (CRTA). Paulik and Paulik [2] produced a similar method which they called quasi-isobaric and quasi-isothermal TA. Sorensen [3] devised stepwise isothermal thermal analysis. Recently we have described a new evolved gas analysis (EGA) system which can perform all of these techniques [4] and was used to compare them under identical experimental conditions. In addition to the established methods mentioned above, we have developed alternative control strategies which have advantages over CRTA in certain applications. There is need for a generic term to describe the ever increasing family of TA techniques in which the reaction determines the heating rate. As there is, as yet, no accepted terminology, in this paper we use the term "rate controlled thermal analysis" (RCTA) to describe all thermal techniques where the heating rate is determined in some way by the rate of reaction or other process. This paper describes some of our RCTA systems and illustrates their application to the study and characterisation of heterogeneous catalysts.

2. Catalysts and thermal techniques

Determination of the identity and concentration of oxidised surface species in metal, or supported-metal, heterogeneous catalysts is frequently of importance. These can be studied by temperature programmed reduction (TPR) in which the uptake of hydrogen from a gas stream is monitored as the sample temperature is linearly raised. Alternatively, the production of water vapour can be monitored. The temperatures of the peaks are used to identify the species and quantitative information is found from the peak areas [5]. It is often found that the peaks are broad and overlap, which can cause problems in identifying their origin and in quantifying the results.

Temperature programmed desorption (TPD) is used to investigate the number and nature of active surface sites. In this technique, gases or vapours are first adsorbed and then desorbed by linear temperature programming. The number of active surface sites is related to the areas of the resulting desorption peaks. Information on the energy of the adsorbate–surface bond can be found from the peak temperatures using the Redhead equation [6]. For example, in the field of aluminosilicate catalysts, the number of Brønsted and Lewis acid sites is of great importance. In principle, the two types of site can be identified and their relative proportions can be found from the TPD of a previously adsorbed base such as ammonia. However, it is not always easy to resolve desorption from the two different sites using conventional linear heating methods.

Temperature programmed reaction gives information on the mechanisms of surface reactions by studying the reaction and desorption of previously adsorbed reactant, intermediate and product molecules as a function of the temperature [7]. Once again, the information yielded by linear heating rates is often limited in terms of resolution.

Thermal methods of analysis (DTA, DSC, TG, EGA, etc.) are frequently the first line of attack in studying the calcination and reduction stages of the preparation of catalysts and their supports, giving information on the temperatures, energies, mass changes and stoichiometry of the processes involved. In many areas, including heterogeneous catalysts, the complex nature of the materials often gives rise to relatively poor resolution.

The vast majority of thermal studies in the field of heterogeneous catalysis employ traditional linear heating rate methods, although there are some exceptions, e.g. the work of Criado et al. [8] on temperature programmed oxidation, and that of Rouquerol and Ganteaume [9] and Barnes and Parkes [10] on catalyst preparation.

3. Equipment

The essence of the new experimental systems is the computer control of the sample temperature which is determined by the reaction rate in a manner dependent on the particular technique employed. The computer is interfaced to gas detectors and furnaces via an analogue-to-digital interface convertor (ADC) and a temperature programmer. We have developed a series of new RCTA control strategies, as well as implementing CRTA, etc.

One version of our EGA systems, using a hygrometer detector, has been described previously [4]. The design has since been developed to incorporate a range of furnances, evolved gas detectors and new control strategies. The various furnace and detector combinations currently possible are illustrated in Fig. 1 and a typical overall system in Fig. 2, which also shows the system feedback loop. In all cases, the monitored level of a selected product gas is used as a measure of the rate of reaction and to control the sample temperature in such a way as to give the desired reaction profile, e.g CTRA.

One configuration uses a thermobalance (Stanton Redcroft TG 750) linked to a magnetic sector mass spectrometer (VG MicroMass 6) via either a jet separator or

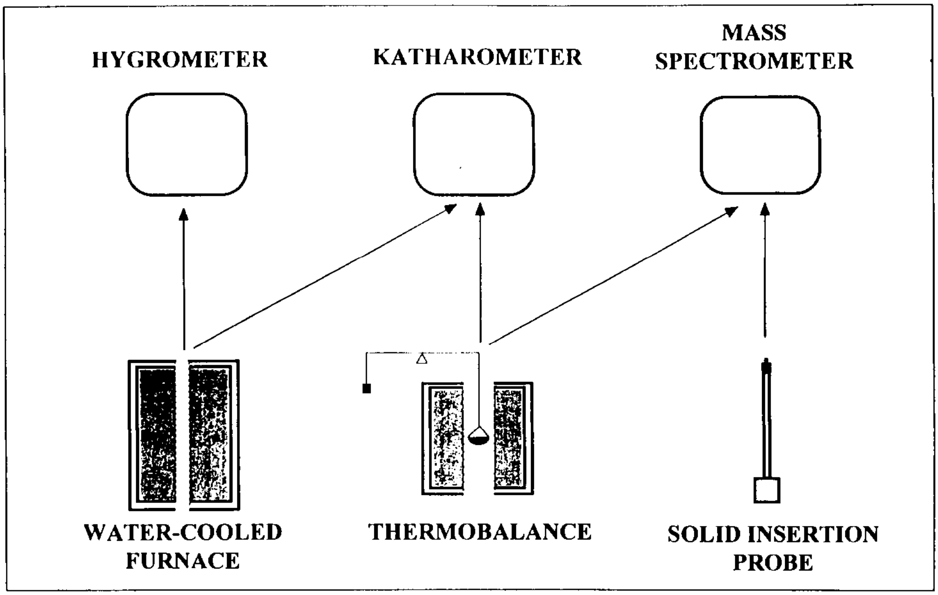

Fig. 1. Combinations of furnaces and detectors used in the RCTA systems.

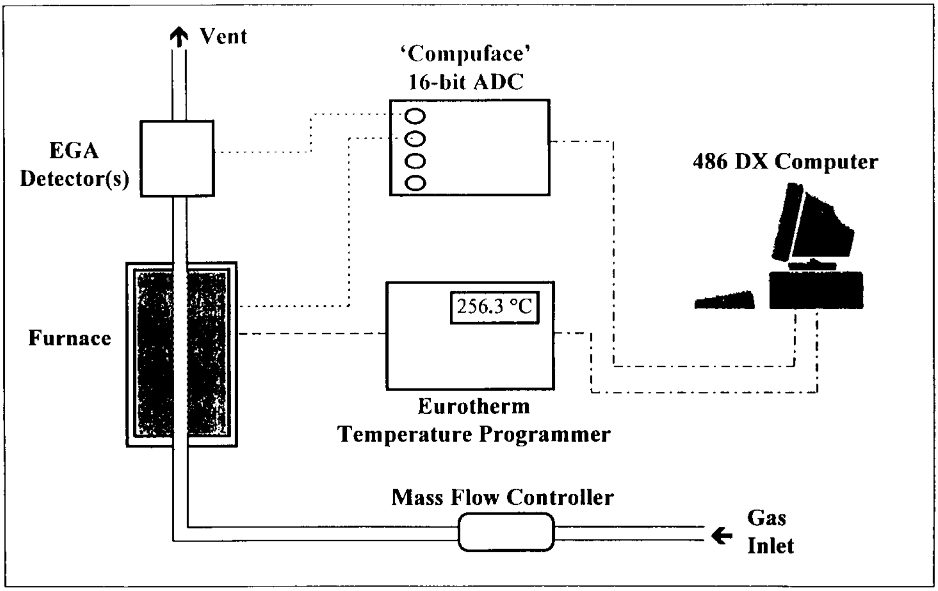

Fig. 2. Schematic diagram of a typical RCTA system, showing the control loop.

a capillary and bypass inlet. The MM6 is a 6 cm radius 90° magnetic sector mass spectrometer with a nominal mass range of 500 a.m.u. and a resolution of 350. Equipped with a four channel peak-select unit, it can control on one product gas while monitoring both this and three others. A more sophisticated design is based on a Stanton Redcroft TG 1000 linked to a VG MicroMass 12 120° magnetic sector mass spectrometer, with a mass range of ca. 1000 and a typical resolution of 1500 a.m.u. The MM12 has a computerised data acquisition and processing system which can be used for off-line multi-channel peak-select work. In conjunction with a hygrometer or katharometer for control purposes, in the mass scanning mode it can follow the simultaneous evolution of any gas or combination of evolved products. This mode of operation is of use in preliminary work to establish which gases are evolved from new samples. The MM12 can also be used to control, in real time, on specific m/z peaks by means of its eight-channel hardware-based peak-select system. With either TG-based system, one advantage is the availability of TG and DTG signals, providing quantitative information of a high precision to supplement that given by the mass spectrometers, which give high accuracy only with careful calibration. The TG-based systems use sample masses in the range 1–30 mg.

Other detectors used include electrolytic hygrometers and two types of katharometer. The hygrometers are especially useful in studying the characterisation of catalysts, as water vapour is frequently a product. One of the katharometers (Gowmac, model type 10-077) uses gold-plated tungsten filaments and is a high sensitivity design, whilst the other employs thermistor detectors and so is more resistant to oxidation, making it more suitable for temperature programmed oxidation work.

There is usually some uncertainty in temperature measurement when using a thermobalance because the thermocouple which measures the sample temperature is not in direct contact with the sample or its container. For some purposes, e.g. TPR or kinetic measurements where accurate temperature measurements is important, this limitation is overcome by using a small furnace (internal dimensions 10 mm × 200 mm), in which the sample crucible, usually a flat-bottomed platinum pan (6 mm × 4 mm) rests on a plate-type thermocouple. This furnace is water-cooled, as are those used in the thermobalances, and so gives the small response time required for good control, even with relatively fast reaction rates.

The systems described above take samples ranging typically from 1–50 mg and, while they can be operated at reduced pressure, are usually run using a purge gas at one atmosphere pressure. In some cases, where diffusion of the product gas limits the rate at which it can be removed from the reaction interface, it is beneficial to operate with very small samples, typically 10–100 μg, and in ultra high vacuum (UHV). This is achieved using a water-cooled solid insertion probe [11] which effectively places the sample (typically a few microgrammes) in the source of the MicroMass 12.

4. Experimental conditions

These are given in Table 1.

Table 1
Summary of experimental conditions[a]

Experiment	Sample	Mass/mg	Method H.R./ °C min^{-1}	Furnace	Detector	Gas flow/cm^3 min^{-1} He
Decomposition	Dolomite	3.6	LH10	WCF	Ka	20
Decomposition	Dolomite	3.6	CRTA	WCF	Ka	20
TPR	V_2O_5	20	LH 5-15	WCF	Hyg	20[b]
TPR	V_2O_5	20	CRTA	WCF	Hyg	20[b]
Rate jump	Dolomite	33	CRTA	WCF	Ka	20
TPD	Clay	0.005	LH 10	SIP	MS	UHV
TPD	Clay	0.005	RCTA-1	SIP	MS	UHV
TP reaction	Clay	15	LH	TG	MS	30
TP reaction	Clay	15	RCTA-2	TG	MS	30
Analysis	$CuSO_4 \cdot 5H_2O$	1.6	LH 5	WCF	Hyg	20
Analysis	$CuSO_4 \cdot 5H_2O$	1.6	RCTA-3	WCF	Hyg	20

[a] Key: H.R. = heating rate; LH = linear heating; WCF = water cooled furnace; SIP = solid insertion probe; TG = thermobalance; Ka = katharometer; Hyg = hygrometer; MS = mass spectrometer; [b] 5% H_2 in He; UHV = ultra high vacuum (no gas flow); CRTA = constant rate thermal analysis.

5. Results and discussion

5.1. *Thermal decomposition of dolomite* ($CaMg(CO_3)_2$)

To demonstrate the capabilities of the system, we show in Fig. 3 (a) a comparison of linear heating rate and CRTA experiments on dolomite, a material which exhibits model behaviour under the conditions chosen. As the height of the evolved gas trace is proportional to the rate of reaction, the difference in reaction rate between the two types of experimental runs is shown dramatically. Fig. 3 (b) shows the data plotted in the form of α (degree of reaction) vs. temperature curves and illustrates the superior resolution obtained with CRTA.

5.2. *Temperature programmed reduction*

Conventional TPR is illustrated in Fig. 4 (a) which shows the reduction of V_2O_5, in an atmosphere of 5% hydrogen in helium, at different heating rates. The TPR profiles are markedly heating-rate dependent, both in terms of the peak temperatures and their areas. This is thought to be due to the different consumption rates and hence concentrations of the hydrogen which, in turn affects the reaction rate. Note that the three curves would show similar total areas if plotted against time, rather than temperature as shown here. The α vs. T curve in Fig. 4(b) may appear unfamiliar but, nevertheless, it gives valuable information. On the same graph is plotted the equivalent linear heating rate experiment which shows that, once again, the CRTA method gives

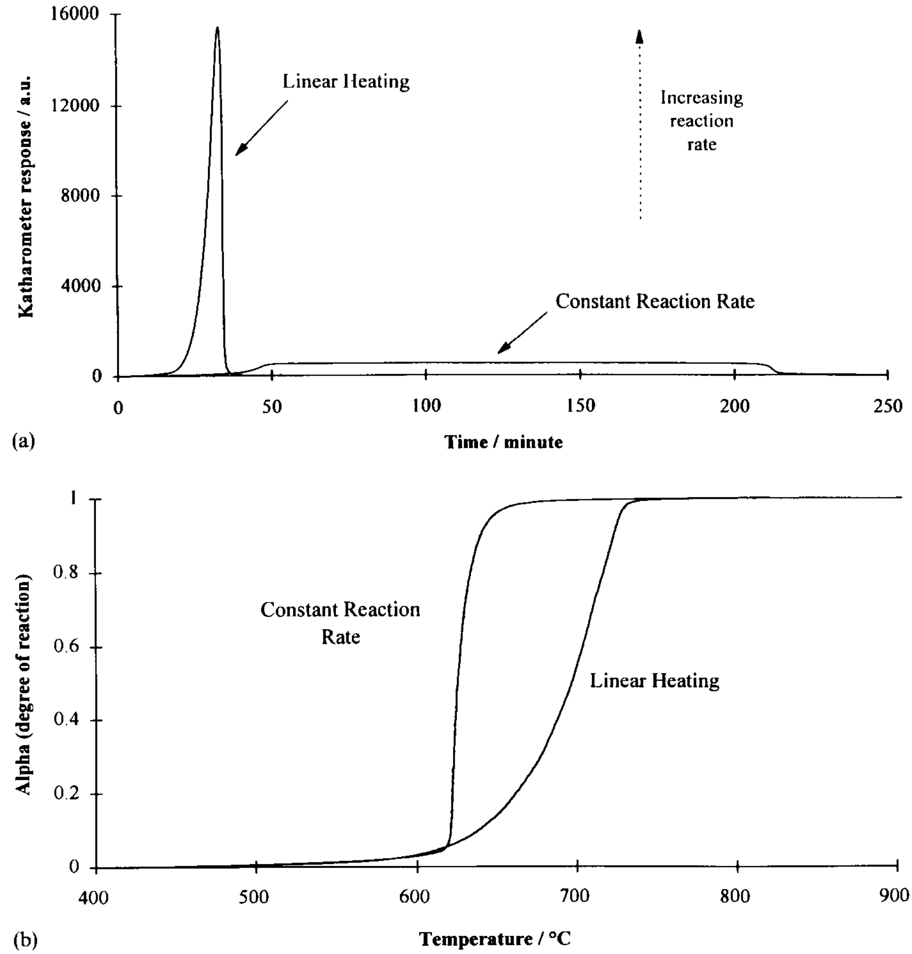

Fig. 3. The thermal decomposition of dolomite under linear heating and constant reaction rate conditions (a), and α vs. temperature plots for the thermal decomposition of dolomite under linear heating and constant reaction rate conditions (b).

better resolution. It is of particular interest to note how far the temperature has to fall to keep the reaction rate constant.

5.3. Determination of the kinetics of thermal decomposition reactions

The advantages of the temperature jump method for establishing the kinetics of thermal decomposition reactions are well known [12]. They can be used to find the activation energy using a single sample under conditions of virtually constant reaction interface and so eliminate many of the variables commonly found in this work. By

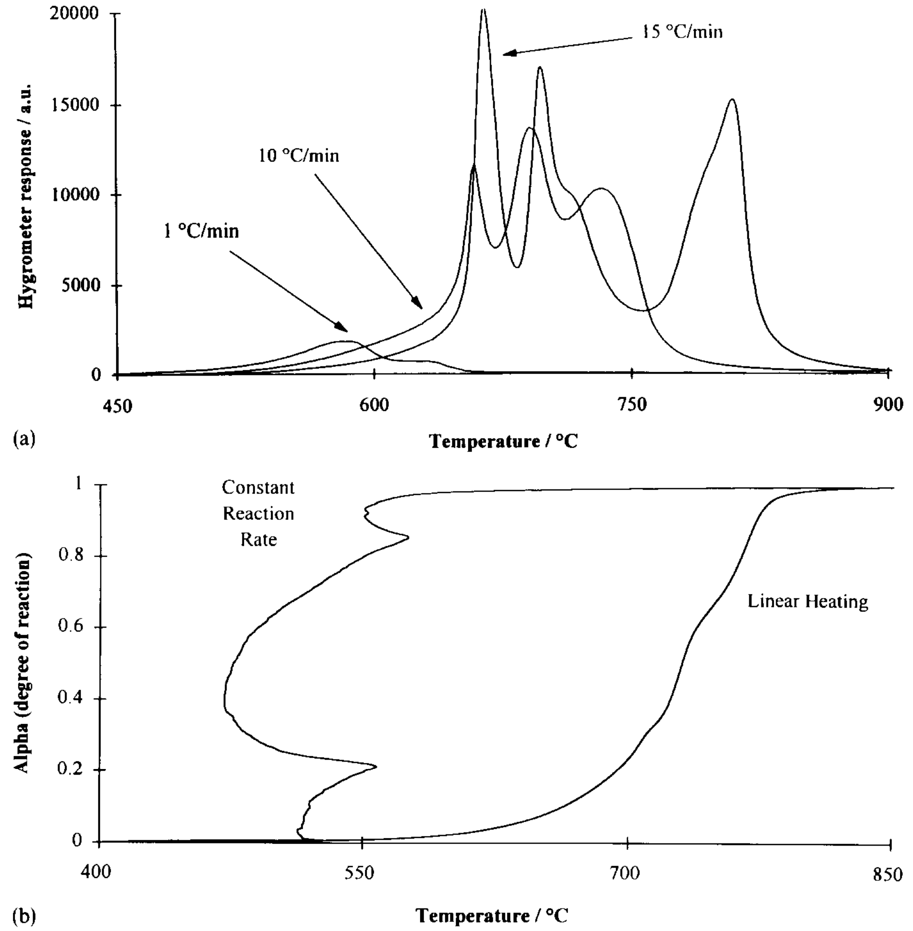

Fig. 4. TPR of V_2O_5 using various linear heating rates (a), and α vs. temperature plots for the TPR of V_2O_5 under linear heating and constant reaction rate conditions (b).

doing the experiment under CRTA conditions the further advantages this technique brings are gained [13]. Fig. 5 shows a variation of the method in which a series of rate jumps is used to study the decomposition of dolomite and the temperature required to maintain the two preset reaction rates is monitored. Although the change in temperature appears small, this is because of the wide temperature range of the experiment and hence the small scale of this axis. It is interesting to note that the temperature required to keep the ratio of the reaction rates constant rises throughout the experiment and this shows another advantage of the technique, namely that it gives a differential activation energy, i.e. it shows how the activation energy varies throughout the course of the process. It is, therefore, more revealing and accurate than the often used isothermal method, in which a series of experiments is done isothermally over a range of

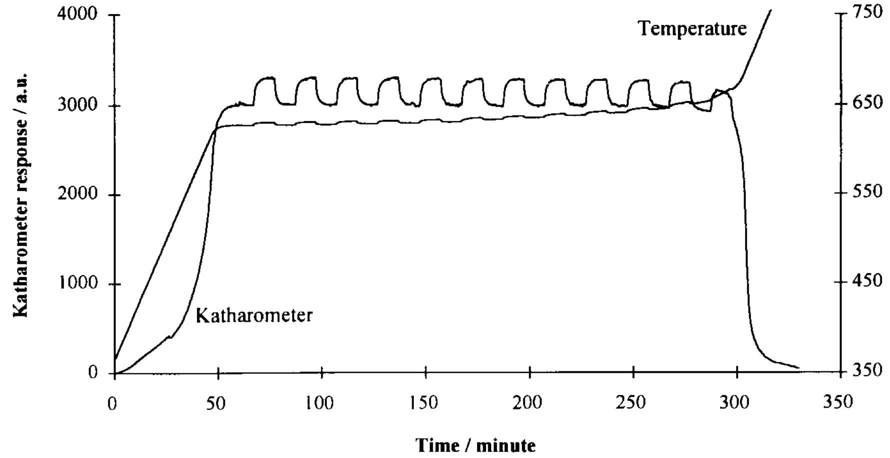

Fig. 5. Rate jump experiment on dolomite under constant reaction rate conditions.

temperatures. Frequently, it is difficult to find a model which covers more than a limited amount of the reaction and so the estimates of the rate constants are subject to error. The method outlined here avoids such problems.

5.4. Temperature programmed desorption

One of the problems with TPD under the usual linear heating rate conditions is the poor resolution often obtained. This is illustrated in Fig. 6 which shows the desorption of cyclohexylamine from an aluminium-exchanged montmorillonite clay, at 10°C $\min^{-1}$ and under RCTA conditions. For this work the solid insertion probe (operating

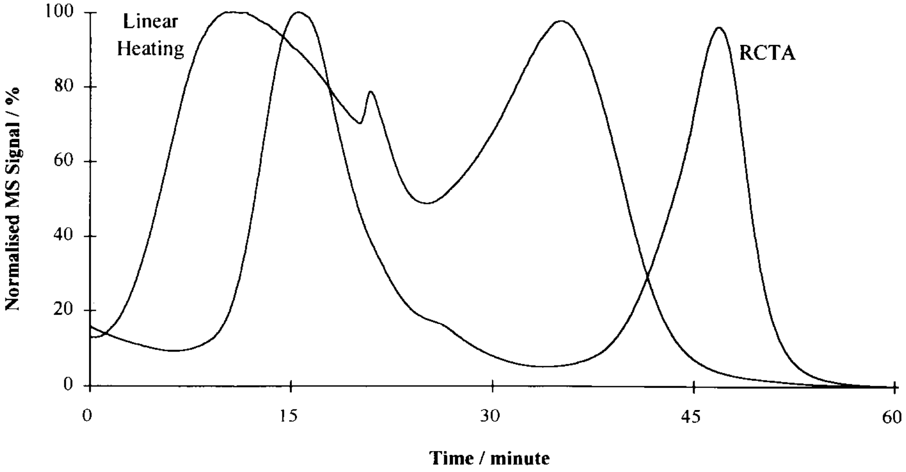

Fig. 6. TPD of cyclohexylamine from an aluminium-exchanged montmorillonite clay under linear heating rate and RCTA conditions.

in UHV) was used to minimise any effects due to diffusion limitations, in conjunction with the MicroMass 12 mass spectrometer. Using a new RCTA algorithm designed specifically for work of this type, the two main desorption events are more clearly resolved.

5.5. Temperature programmed reaction

A conventional temperature programmed reaction experiment on the catalytic dehydrogenation of propan-2-ol on an acid-activated Clophill clay is shown in Fig. 7(a). The propan-2-ol peak represents desorption of unreacted material and the

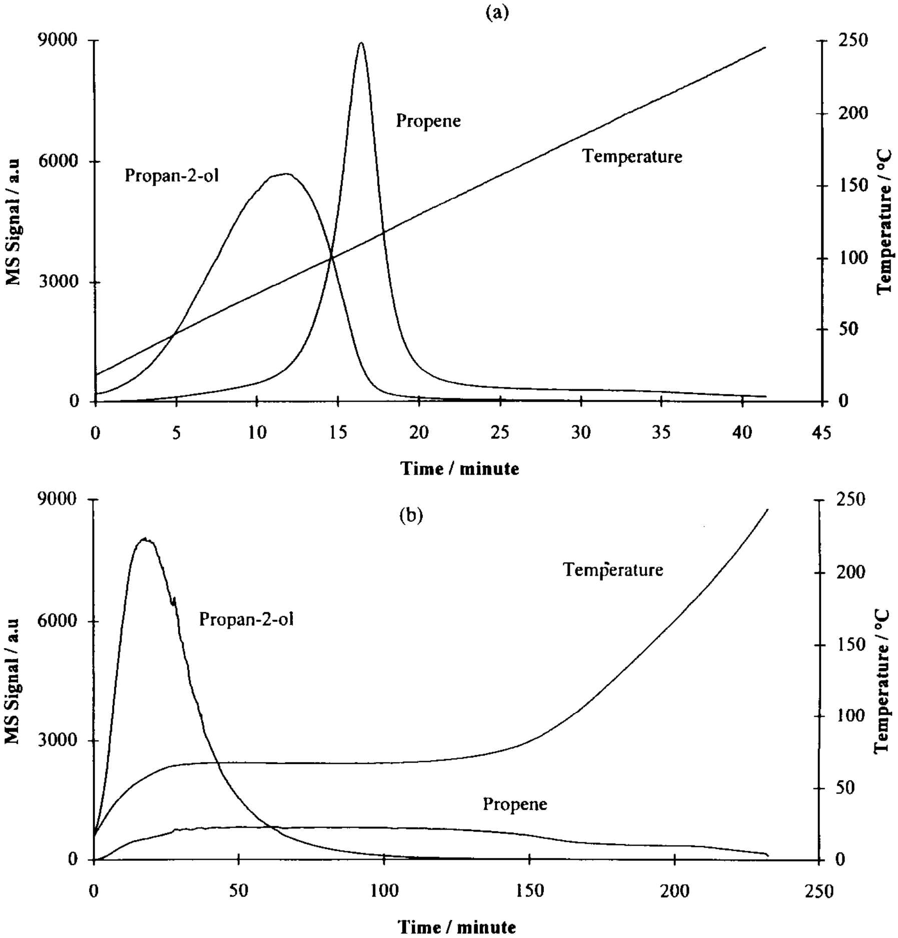

Fig. 7. Temperature programmed reaction of propan-2-ol on an acid activated Clophill clay: (a) using a linear heating rate; and (b) using an RCTA method.

propane trace shows how the reaction is proceeding. The serious overlap between the peaks shows the advantages of MS over TG which would only have given the overall mass loss and so would have been meaningless. The corresponding RCTA experiment, which in this case was set to control on the rate of propene evolution, shows better resolution (Fig. 7(b)) and makes it possible to study the mechanism in more detail.

5.6. Analytical applications using an enhanced resolution algorithm

The use of a further RCTA algorithm developed to provide enhanced resolution in analytical applications is illustrated in Figs. 8 (a) and 8 (b) which show the EGA traces of the thermal decomposition of copper sulphate pentahydrate. The former used

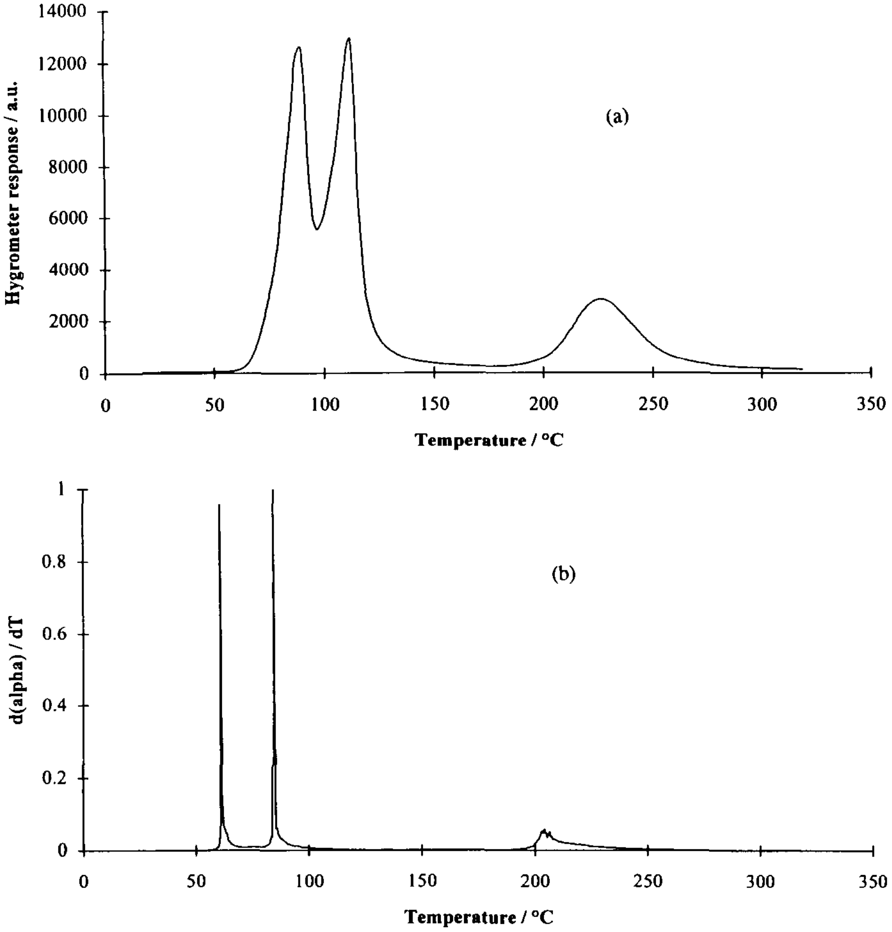

Fig. 8. EGA analysis of copper sulphate pentahydrate: (a) using a linear heating rate, and (b) using an RCTA method.

a linear heating rate of 5°C $\min^{-1}$, while the latter used an algorithm which limits the heating rate to between 0.01°C $\min^{-1}$ and 5°C $\min^{-1}$. It must be admitted that the excellent resolution of the latter is due in part to the presentation of the data in the temperature domain. Nevertheless, we believe this approach is valid, providing the operational parameters are made clear.

6. Conclusions

The evolved gas analysis systems described here offer significant improvements in a number of areas over the standard thermal techniques used to characterise catalysts. Clearly there is considerable scope for applications in many other areas of chemistry and materials science.

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References

[1] J. Rouquerol, Thermochim. Acta, 144 (1989) 209.
[2] J. Paulik and F. Paulik, Thermochim. Acta, 100 (1986) 23.
[3] O.T. Sorensen, Thermochim. Acta, 50 (1982) 263.
[4] P.A. Barnes, G.M.B. Parkes and E.L. Charsley, Anal. Chem., 66 (1994) 2226.
[5] N.W. Hurst, S.J. Gentry and A. Jones, Catal. Rev. Sci. Eng., 24 (2) (1982) 233.
[6] P.A. Redhead, Trans. Faraday Soc., 57 (1961) 641.
[7] K.C. Waugh, Appl. Catal., 43 (1988) 315.
[8] C. Real, M.D. Alcala, and J. Criado, J. Therm. Anal., 38 (1992) 797.
[9] J. Rouquerol and M. Ganteaume, J. Therm. Anal., (1977) 201.
[10] P.A. Barnes and G.M.B. Parkes, Proc. 6th Int. Symp. on the Scientific Bases for the Preparation of Heterogeneous Catalysts, Louvain-la-Neuve, 1994, in press.
[11] P.A. Barnes and G.M.B. Parkes, J. Therm. Anal., 39 (1993) 607.
[12] J.H. Flynn, J. Therm. Anal., 2 (1962) 1111.
[13] J. Rouquerol, S. Bordère and F. Rouquerol in W. Smykatyz-Kloss and S.St.J. Warne (Ed.), Thermal Analysis in the Geosciences, Springer, 1991, p. 134.