

APPLICATION OF SCTA TO THE STUDY OF THE REACTIVITY OF ACID-BASE CATALYSTS

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Conventional thermal methods for studying heterogeneous catalyst systems are based on pre-set linear heating rates. Techniques such as temperature programmed thermolysis, reduction, oxidation, desorption and reaction provide important information on the formation, surface properties and reactivity of catalysts. The approach of ‘sample controlled thermal analysis’ (SCTA) can be applied successfully to overcome the principal limitations of the conventional forms of these methods [1].

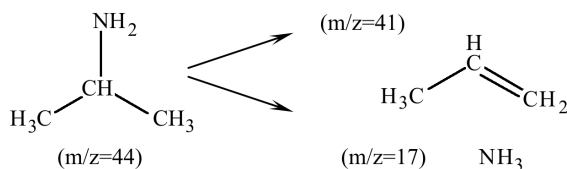
Most, if not all, catalysts are characterised by the heterogeneity of their surface, i.e. the type and amount of active centres, which can be identified by specific surface-catalysed reactions. Thermal methods are widely used for this purpose, as the temperature at which a particular event occurs reflects the apparent activation of the rate-limiting step of the surface-catalysed process and so provides direct information on the reactivity of active centres. However, the diffusion of gases from micropores, found in porous catalysts, can be rate determining, with the desorption/reaction of the products no longer being the observed rate limiting step. Thus, the internal pressure build-up can affect the rate of removal of product and hence the observed rate and temperature of the process. SCTA, where the sample temperature is changed to specifically control the reaction rate throughout a whole process, offers a number of advantages over conventional linear heating methods by minimising temperature and concentration gradients in the sample and reducing the effects of diffusion [2].

Zeolites are widely used porous acid-base materials whose catalytic behaviour depends on the number and nature of the surface functional groups. The interaction of the materials with a specific reactant is often used for characterising the density of the active centres of these catalysts. However, as the processes at heterogeneous surfaces are complex, careful control of the environment using the SCTA approach provides a new insight into the number and nature of active surface sites and also to the mechanisms of the processes involved [3].

Alkylamines are a sensitive probe for estimating the acidity of zeolites. For example, isopropylamine desorbs unreacted from Lewis sites but decomposes to propene and ammonia at Brønsted acid sites, via the Hoffman elimination reaction [4].

As can be seen in Fig. 1, conventional linear heating causes not only problems in obtaining qualitative data due to diffusion limitations in pores but also makes it very

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Scheme 1

difficult to get quantitative information, as the two processes, i.e. the desorption of isopropylamine from Lewis sites and the Hoffman elimination reaction, strongly overlap. Under SCTA conditions, the underlying rate of the first event, i.e. the physical desorption of unreacted adsorbate, can be kept low enough to allow it to reach virtual completion before the consequent surface-induced reaction starts, making it possible to separate it from the other surface processes occurred at the zeolite.

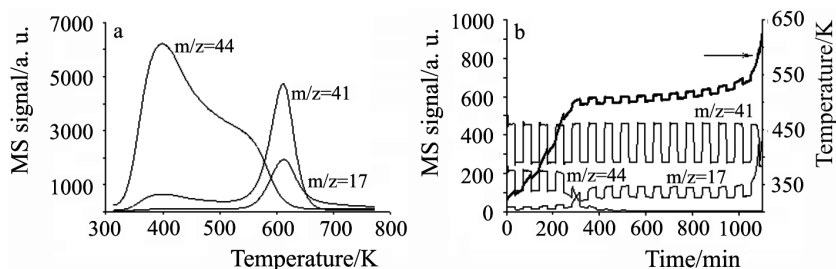
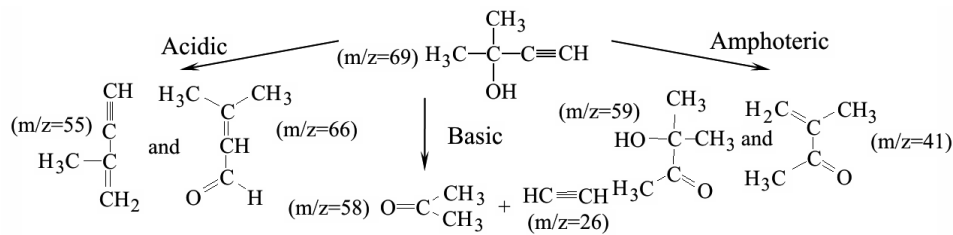


Fig. 1 Desorption and reaction of a – isopropylamine on HY zeolite using conventional linear heating and b – SCTA: ($m/z=44$) isopropylamine, ($m/z=17$) ammonia and ($m/z=41$) propene

2-methyl-3-butyn-2-ol is a more sensitive probe than isopropylamine as it reacts selectively over a wider range of catalyst functionalities, and so is used to probe surface heterogeneity [5].



Scheme 2

In a conventional linear heating procedure (Fig. 2), two principal reactions occur at the acid and amphoteric sites, which are characterised by different reaction rates, and, hence, diffusion laws. In SCTA experiments such problems are eliminated and, moreover, there is the significant (and reproducible) temperature variation at ca. 500 K, accompanied by an increase in the signal of the product of the reaction catalysed by basic

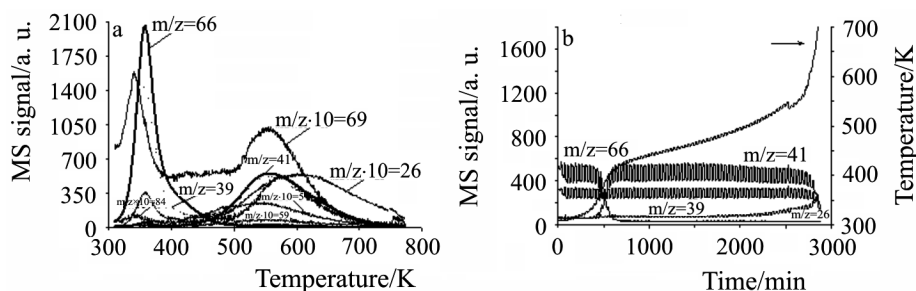


Fig. 2 Reactions of a – 2-methyl-3-butyn-2-ol at HY zeolite using linear heating and b – SCTA: $m/z=26$ (acetylene), $m/z=39$ (controlled fragment), $m/z=41$ (3-methyl-3-butene-2-one), $m/z=58$ (acetone), $m/z=59$ (3-hydroxy-3-methyl-2-butanone), $m/z=66$ (2-methyl-1-buten-3-yne), $m/z=69$ (2-methyl-3-butyn-2-ol) and $m/z=84$ (prenal)

sites. This feature does not appear in the conventional linear heating procedure, demonstrating the sensitivity of SCTA techniques towards this catalytic reaction. Hence, this process in a controlled environment is noteworthy not just because of the decreased influence of temperature and concentration gradients that result in an enhanced resolution but also because of the additional information obtained on the reactivity of catalytic centres.

The application SCTA to the study of reactivity enables a greater control over the reaction environment and so provide results that are less liable to contain artefacts due to heat and mass transfer effects. This approach enhances the resolution of overlapping events, provides a greater insight into the nature of the mechanism of the reaction and reveals the lowest temperature ranges over which the process can occur. Moreover, SCTA (rate jump method [6]) facilitates the calculation of the apparent activation energies of the processes without requiring any prior knowledge of specific kinetic models (Figs 1, 2b). This enables the determination of the reactivity of the catalyst as a function of surface coverage, so revealing the distribution of the energy and hence of the reactivity of the active sites [7].

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