

Comparative test of procedures for thermal desorption analysis

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Simulated thermal desorption spectra have been used to test the performance of several analysis procedures for obtaining the correct activation energy as a function of adsorbate coverage. The so-called complete method and the leading edge analysis give reliable results. The use of approximate methods, however, which are based on peak maximum temperatures and/or peak width, should be avoided.

Introduction

Thermal desorption spectroscopy (TDS) is one of the most frequently employed techniques in surface science. It is used to determine adsorbate coverages, and to evaluate activation energies of desorption.

The rate of desorption r at adsorbate coverage θ is described by:

$$r(\theta) = -d\theta/dt = \nu(\theta) \theta^n \exp(-E(\theta)/RT) \quad (1)$$

in which t is the time, ν the pre-exponential factor of desorption, n the order of desorption, E the activation energy of desorption, R the gas constant and T the temperature. The relation between T and t is given by $dT/dt = \beta$, in which β is the heating rate. Lateral interactions between adsorbate particles can cause E and ν to depend on coverage.

Several procedures have been proposed for the evaluation of the desorption parameters from thermal desorption spectra, see Falconer and Schwartz for a review¹. In this paper we compare the performance of these procedures on simulated thermal desorption spectra, for which the desorption parameters $E(\theta)$, $\nu(\theta)$ and n are exactly known.

Analysis procedures

The complete analysis, based on the rigorous application of equation (1), uses Arrhenius plots of $\ln(r)$ vs T^{-1} for fixed coverages, taken from a family of thermal desorption curves².

The Habenschaden-Küppers or 'leading edge' analysis determines $E(\theta)$ from an Arrhenius plot constructed from the leading edge of the thermal desorption spectrum, where θ can be considered constant³. Redhead's peak maximum method relates the peak maximum temperature T_m via an assumed value for ν to the desorption energy E by $E = RT_m \times [\ln(\nu T_m/\beta) - 3.46]$, provided the desorption follows first order kinetics⁴. The Chan-Aris-Weinberg equations express $E(\theta)$ and $\nu(\theta)$ in terms of the peak maximum temperature T_m , and the peak width, either at half or at three-quarter of the maximum intensity⁵. The Falconer-Madix method uses sets of spectra corresponding to the same initial coverage but taken at different heating rates. A logarithmic plot of either the peak height I or β/T_m^2 vs T_m^{-1} gives a straight line with slope equal to $-E/R$.⁶

Simulated spectra

Spectra corresponding to first-order kinetics have been simulated by solving equation (1) with a Runge-Kutta method⁷. We assume that E varies linearly with θ as $E(\theta) = E_0 - W \cdot \theta$ with $E_0 = 100 \text{ kJ mol}^{-1}$ and $W = 10 \text{ kJ mol}^{-1}$. This simulates the existence of pair-wise repulsive interactions between the adsorbed particles. We assume furthermore that $\log \nu$ varies linearly with coverage such that $\nu = 10^{14} \text{ s}^{-1}$ at $\theta = 0$ and about 10^{12} s^{-1} at $\theta = 1$. The heating rate is 1 K s^{-1} . In order to test the Falconer-Madix procedures, additional spectra have been simulated with five different heating rates between 0.1 and 10 K s^{-1} .

Test results

Figure 1 shows $E(\theta)$ as determined from the simulated spectra with the different procedures for TDS analysis. The heavily drawn line represents $E(\theta)$ used as input for the simulation.

As Figure 1 shows, the complete method and the leading edge or Habenschaden-Küppers method yield an excellent reproduction of the correct $E(\theta)$ values. Only at low coverages small and hardly significant deviations occur, which are mainly due to the limited number of points used in the calculations.

The Falconer-Madix procedures, based on variation of the heating rate, give $E(\theta)$ values that deviate somewhat from the true values. The method using peak maximum temperatures produces slightly better results than the one using peak amplitudes. Nevertheless, the deviations are relatively small and the trend in $E(\theta)$, i.e. falling with increasing coverage, is satisfactorily reproduced.

The simple methods, based either on the peak maximum temperature or on the combination of peak maximum and width, perform rather poorly. Application of the Redhead formula with a chosen pre-exponential of 10^{13} s^{-1} gives $E(\theta)$ values which deviate significantly from the true value. Also, the trend in $E(\theta)$ is not correctly reproduced.

The largest deviations of $E(\theta)$ from the correct value are found by applying the Chan-Aris-Weinberg formulae, as Figure 1 clearly shows. Note, however, that extrapolation of the calculated $E(\theta)$ data to $\theta = 0$ yields approximately the correct activation energy of desorption at zero coverage. Hence the merit of the Chan-Aris-Weinberg method is that it provides a rapid and reliable determination of E_0 when a series of thermal desorption spectra corresponding to different initial coverages is available.

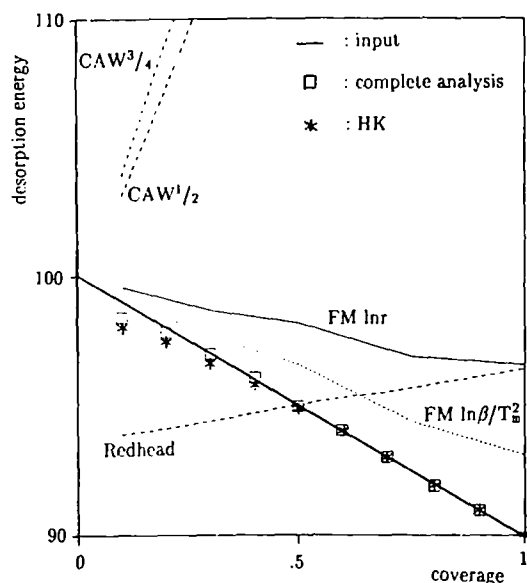


Figure 1. Test results of thermal desorption analysis: activation energies of desorption (in kJ mol^{-1}) as a function of coverage (in fraction of a monolayer) as determined with several procedures from simulated thermal desorption spectra. CAW: Chan-Aris-Weinberg analysis, based on peak widths taken at half and three-quarter peak intensity; FM: Falconer-Madix analysis, based on varying the heating rate; HK: Habenschaden-Küppers or leading edge analysis. See the text for a brief outline of the methods tested.

Conclusion

Thermal desorption analysis should preferably be carried out by complete methods such as those described by King² and by Habenschaden and Küppers³. The Falconer-Madix method⁶ which is based on peak positions as a function of heating rate produces desorption energies with a small, in practice probably acceptable, error. The methods based on peak maximum temperature and peak width, however, should be avoided, with the exception that the Chan-Aris-Weinberg method⁵ correctly yields the E at zero coverage. The trends in $E(\theta)$ at non-zero coverage, however, are entirely without meaning.

A full report of this work, including tests of procedures to derive desorption orders, activation energies and pre-exponential factors from simulated first and second order thermal desorption spectra will be published elsewhere⁸.

References

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