Influence of Re-adsorption and Surface Heterogeneity on the Microkinetic Analysis of Temperature-Programmed Desorption Experiments

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A profound microkinetic analysis of the influence of re-adsorption and of surface energetic heterogeneity on temperature-programmed desorption (TPD) experiments is performed on the basis of the Wigner−Polanyi equation. Exact solutions for TPD experiments under both re-adsorption-free and re-adsorption-dominated conditions from energetically homogeneous surfaces are presented. TPD experiments from energetically heterogeneous surfaces with uniform energy distribution are analyzed considering the surface diffusion of adsorbates. Convenient mathematical approaches are derived to evaluate the TPD profiles for first-order and second-order desorption. It is shown that, when the heterogeneity is strong and the coverage is not close to 0 or 1, the slope in the plot of $\ln(T_p/\beta)$ versus $1/(RT_p)$ yields the differential heat of adsorption for freely occurring re-adsorption at $\Theta = \Theta_p$. In the absence of re-adsorption, the differential desorption energy at $\Theta = \Theta_p$ can be derived from the slope. Two case studies show that the thermodynamic parameters, especially the surface energy distribution, can be obtained successfully from TPD experiments based on the derived methods.