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DIFFUSION AND READSORPTION EFFECTS DURING TPD FROM POROUS MATERIALS

E. TRONCONI, L. LIETTI, P. FORZATTI

Dipartimento di Chimica Industriale ed Ingegneria Chimica "G. Natta" del Politecnico, Piazza Leonardo da Vinci 32,
I-20133 MILANO

ABSTRACT

A model is presented which accounts for the coupled effects of intraparticle diffusion and readsorption during TPD from porous materials. This model has been validated by simulating the experiments of methanol TPD from γ-Al_2O_3. Inspection of the groups of variables identified by dimensional analysis provides guidance for the optimal choice of the TPD operating conditions.

INTRODUCTION

Temperature Programmed Desorption technique is widely used for the characterization of porous materials, specifically in the field of catalysis. In principle, methods of analysis of TPD traces are able to provide a complete description of the desorption kinetics [1], from which information concerning the interaction of chemical species and catalytic surface can be derived, possibly in combination with additional techniques, such as FTIR [2]. However, a number of recent papers pointed out that interpretation of TPD data may be complicated by the coupled effects of intraparticle diffusional resistances and readsorption of the desorbed species [3]. The relevance of such effects has been addressed both experimentally and theoretically in our laboratory. The present paper provides a survey of our activity in this area.

THEORY

The general conservation equations for TPD from a bed of spherical particles into a flowing carrier gas are written below for a linear heating schedule in non dimensional form along with associated initial and boundary conditions [2]:

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$$\frac{\partial \theta}{\partial \tau} = 3 \frac{v_m W_c k_a}{\rho_c Q} \gamma - (k_d \frac{\Delta T}{\beta}) \theta \qquad (1)$$

$$\varepsilon_p \frac{\beta R_p^2}{D_p T} \frac{\partial \gamma}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} (\rho^2 \frac{\partial \gamma}{\partial \rho}) - \frac{Q \rho_c R_p^2}{3 W_c D_p} \frac{\partial \theta}{\partial \tau} \qquad (2)$$

$$\frac{\varepsilon_b}{(1-\varepsilon_b)} \frac{W_c \beta}{Q \Delta T \rho_c} \frac{\partial \gamma^\circ}{\partial \tau} = - \gamma^\circ + \frac{3 W_c D_p}{Q \rho_c R_p^2} (- \frac{\partial \gamma}{\partial \rho} \Big|_{\rho=1}) \qquad (3)$$

$$\tau = 0 \qquad \theta = 1 \qquad 0 \le \rho \le 1 \qquad (4)$$

$$\begin{array}{lll} \tau = 0 & \gamma = 0 & 0 \le \rho \le 1 \\ \rho = 0, \ \tau > 0 & & \dfrac{\partial \gamma}{\partial \rho} = 0 \\ \rho = 1, \ \tau > 0 & & \gamma = \gamma^\circ \end{array} \qquad (5)$$

$$\tau = 0 \qquad \gamma^\circ = 0 \qquad (6)$$

For homogeneous surfaces, the expression of the rate constant for desorption is written as $k_d=k_d^\circ \exp(-E_d/RT)$. Definition of the variables appearing in Eqs. (1-6) are given in the notation. Equation (1) is the adsorbate mass balance on the solid surface. Equations (2) and (3) represent the mass balances of the adsorbate in the gas phase inside the catalyst pores and in the catalyst bed, respectively. The following assumptions have been made: i) linear adsorption-desorption kinetics ($r_d=k_d\theta$; $r_a=k_aC$); ii) non activated adsorption rate constant; iii) negligible interphase diffusional limitations; iv) isothermal CSTR model for the catalyst bed. All of these hypotheses appear to be reasonable for our typical TPD operating conditions.

The following dimensionless groups of parameters governing the TPD process are identified: 1) $\psi_1=(\beta R_p^2/D_p \Delta T)$, ratio of the characteristic time for internal diffusion ($t_D=R_p^2/D_p$) to the characteristic time of the TPD experiment ($t_{TPD}=\Delta T/\beta$); 2) $\psi_2=(\beta W_c/ \Delta T Q \rho_c)$, ratio of the characteristic time for convective removal of the desorbed species ($t_{CR}=W_c/Q\rho_c$) to the time of the TPD run; 3) $\Phi_1=(\rho_c Q R_p^2/3W_c D_p)$, ratio of the characteristic time for internal diffusion to the characteristic time for convective removal; 4) $\Phi_2=(v_m W_c k_a/ \rho_c Q)$, ratio of the time for convective removal to time for readsorption ($1/(v_m k_a)$).

Under typical TPD operating conditions ($t_{TPD}+40$ min, t_D+10^{-2} min, $t_{CR}+10^{-3}$ min) both ψ_1 and $\psi_2 \ll 1$. Accordingly the terms in the LHS of eqs. (2) and (3) are negligible, which implies that there is no build up of the adsorbate either inside the catalyst pores or in the TPD reactor.

MODEL VALIDATION

The capability of the TPD model given above to predict the effects of internal mass transfer limitations and readsorption has been determined by simulating experiments of methanol TPD from γ-Al_2O_3. The kinetic parameters for adsorption and desorption were estimated by running TPD experiments with different carrier gas rates and catalyst loads with small solid particles, for which the absence of intraparticle diffusional limitations had been experimentally demonstrated [4]. In this diffusional-free regime a linear relationship holds between $\theta/C°$ and $\rho_c Q/v_m W_c$, i.e. $\theta/C° = (1/k_d)*(\rho_c Q/v_m W_c) + k_a/k_d$. Fig. 1 shows isothermal characteristic plots of $\theta/C°$ against $\rho_c Q/v_m W_c$ at different temperatures for methanol TPD from γ-Al_2O_3. Analysis of the slopes of the corresponding plots and of the associated intercepts yielded k_a and k_d. The effective diffusivity D_p was estimated a priori. The model was proved to simulate effectively the growth of the temperature of the TPD peak maximum (T_M) and the drop of the effective desorption rate constant (k_{eff}) on increasing Φ_1 beyond a critical value, as shown in Fig.2.

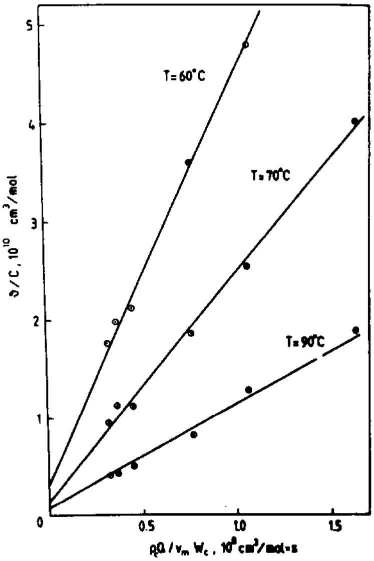

Fig. 1 - Isothermal characteristic plots for determining k_a and k_d.

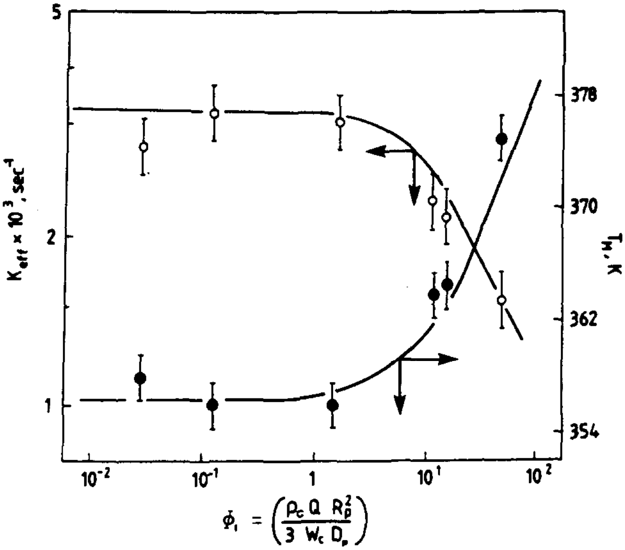

Fig. 2 - Plot of k_{eff} (open circles) and T_M (full circles) versus Φ_1. Solid lines represent model predictions.

EXPERIMENTAL CRITERIA FOR ASSESSING THE RELEVANCE OF INTRAPARTICLE DIFFUSION AND READSORPTION

It is worth noting that changes in T_M and in k_{eff} as functions of R_p (Fig.2) provide an experimental criterion to detect the presence of intraparticle diffusional intrusions during TPD experiments. Besides, the significance of readsorption can be established by running TPD experiments in a diffusion-free regime with different values of Q and W_c, according to the procedure described in the previous section. Indeed, the limiting behaviours corresponding to negligible readsorption and to equilibrated readsorption would result in straight lines passing through the origin ($k_a/k_d=0$), and in horizontal lines ($\Theta/C°=k_a/k_d$), respectively (Fig.1).

MODEL ANALYSIS

The coupled effects of intraparticle diffusion and readsorption were analyzed by solving eqs. (1-3) for pseudo steady-state conditions and for a wide range of values of Φ_1 and Φ_2 [5]. Results are plotted in Fig. 3 in terms of k_{eff}/k_d vs Φ_1, with Φ_2 as a parameter. The following remarks are worthy of note.

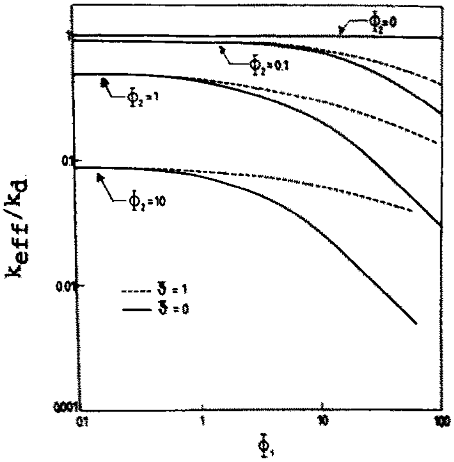

Fig. 3 - Coupled effects of internal diffusion and readsorption.

1) When Φ_1 is small no gradients exist in the gas phase and the rate of desorption is controlled by readsorption, $k_{eff}=k_d/(1+\Phi_2)$.

2) As Φ_1 increases, diffusional limitations become manifest and k_{eff}/k_d decreases with growing Φ_1.

3) The extent of variation of k_{eff}/k_d depends on Φ_2: it is nil when $\Phi_2=0$, and is more apparent as Φ_2 increases. Strong intraparticle gas-phase concentration profiles develop in the case of negligible readsorption ($\Phi_2=0$) as Φ_1 increases. However the concentration at the catalyst edge remains the same, so that the shape of the TPD curve is not affected. This indicates that the existence of strong intraparticle C-gradients ($\Phi_1>1$) is only a necessary but not a sufficient condition for the TPD experiments to be affected by diffusional intrusions. C-gradients only indirectly slow down desorption by causing a buildup of adsorbate within the particle, which enhances the local rate of readsorption, when $\Phi_2>0$.

4) For fixed Φ_1 and Φ_2, k_{eff}/k_d is also a function of θ in the diffusion-controlled regime: k_{eff}/k_d changes during the TPD run, and tends to a minimum when complete depletion of the desorbing surface is approached at the end of the TPD experiment.

It has also been shown that the same results of Fig.3 hold in the case of heterogeneous surface with a linear θ-dependence of the desorption energy [6].

Inspection of the variables identified by dimensional analysis provides guidance for the optimal choice of the TPD operating conditions. Under typical TPD conditions $\psi_1 \ll 1$ and $\psi_2 \ll 1$ so that accumulation of the adsorbate either in the catalyst pores or in the catalyst bed is prevented.

Internal concentrations gradients are controlled by Φ_1. In order to avoid diffusional intrusions one wants to make Φ_1 small. This can be accomplished by reducing Q and R_p, and by increasing W_c. However, a great catalyst load may prevent a CSTR treatment of the TPSR data, whereas a low flow rate slows down interphase transport. Furthermore, both increasing W_c and reducing Q favors the readsorption of the desorbed species, as reflected by greater Φ_2 values. It seems then that the size of the catalyst particles should be minimized. Due to the very limited bed depth, this does not result in significant pressure drops anyway.

NOTATION

C, C°	gas phase concentration of desorbed species within the pellet and in the reactor, respectively (mol/cm^3)
D_b	effective bed diffusivity (cm^2/s)
D_p	effective particle diffusivity (cm^2/s)
E_d	activation energy for desorption (Kcal/mol)
k_a	adsorption rate constant (cm^3/mol s)
k_d	desorption rate constant (s^{-1})
k°_d	pre-exponential factor for desorption (s^{-1})
k_{eff}	effective desorption rate constant (s^{-1})
Q	flow rate of carrier gas (cm^3/s)
r	radial coordinate (cm)
r_a	rate of readsorption
r_d	rate of desorption
R	gas constant
R_p	average particle radius (cm)
t	time (s)
T	temperature (K)
T°	initial temperature of TPD run (K)
T_M	temperature of the TPD peak maximum
v_m	initial surface concentration of adsorbate (mol/cm^3)
W_c	catalyst mass (g)
β	heating rate (K/s)
γ, γ°	dimensionless gas-phase concentration within the pellet and in the reactor, respectively
ΔT	temperature range of TPD run (K)
ϵ_b	void fraction of catalyst bed
ϵ_p	void fraction of catalyst particle
θ	surface concentration of adsorbate
θ°	initial surface concentration of adsorbate
$\rho=(r/R_p)$	dimensionless radial coordinate
ρ_c	density of catalyst pellet (g/cm^3)
$\tau=(\beta t/\Delta T)$	dimensionless run time
Φ_1	modulus for diffusion effects
Φ_2	modulus for readsorption effects
ψ_1	modulus for build up in the pellet
ψ_2	modulus for build up in the bed

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