Experimental Criteria for Diffusional Limitations during Temperature-Programmed Desorption from Porous Catalysts

The existence of strong intraparticle diffusional limitations during temperature-programmed desorption (TPD) has become a major concern in the last few years. Herz et al. (1) observed significant differences between the shape of their TPD curves of CO from porous $Pt/\gamma-Al_2O_3$ and the spectra obtained by other workers using different operating conditions. By means of a mathematical model they explained their results showing how severe resistances to the diffusion of CO in the pores of the sample, coupled with readsorption, can modify the features of the TPD curve. Gorte (2) applied dimensional analysis to the TPD model equations given in (1), and identified the groups of catalyst parameters governing the main effects in the TPD process, including lag times, accumulation in the cell, diffusion, and readsorption. In particular, he found that the presence of intraparticle concentration gradients is controlled by the ratio of the rate of adsorbate removal from the cell to the rate of internal diffusion. For a single catalyst pellet such a ratio is represented by (Ql/DS), where Q is the volumetric gas flow rate out of the cell, l the thickness of the catalyst sample, D the effective diffusivity, and S the external geometric area of the sample. Proposed criteria to predict the onset of mass-transfer limitations suggest that intraparticle gradients are negligible if $(Ql/DS) < 0.1$, while pore diffusion governs TPD when $(Ql/DS) > 20$. Gorte's conclusion is that, for a single particle, it may be difficult to find feasible operating conditions where the first inequality is satisfied. A recent paper (3) has extended the modeling approach to the case of TPD from a bed of porous spherical catalyst particles, simulating the effects of particle size, flow rate, and catalyst mass upon the shape of the TPD curves. It should be recognized, however, that the risk of oversimplification is easily associated with modeling of TPD experiments, due to the superposition of several physicochemical phenomena and the numerous parameters involved. So far, no experimental investigation aimed at demonstrating the effects of intraparticle diffusion on TPD has been reported in the literature. An experimental approach seems valuable, though, as it can: (1) clarify whether one can possibly obtain quantitative chemical information, not disguised by diffusional effects, in the case of TPD from porous catalysts; (2) provide verification of the existing a priori criterion for the onset of diffusional intrusions; and (3) validate the available theoretical treatments. This paper addresses the points above, and presents the results of methanol TPD from porous $\gamma-Al_2O_3$ covering a wide range of catalyst particle radii.

THEORY

To fix the ideas, we refer in the following to a TPD experimental system where the sample cell is well mixed and isothermal, and the catalyst bed is differential both in concentration and temperature. Homogeneity of the desorbing surface is assumed. Intraparticle mass transfer is rate controlling, and local readsorption equilibrium is established according to a linear isotherm. Under the above assumptions, and for spherical catalyst particles of average radius R_p, the following approximate expres-

sion for the overall observed rate of desorption applies (2),

$$-\frac{d\bar{\theta}}{dt} = \pi^2 \frac{D}{\alpha\rho R_p^2 K} \bar{\theta}. \qquad (1)$$

In Eq. (1) D is the effective diffusivity of the desorbing species, $\bar{\theta}$ is the average fractional surface coverage, $\alpha\rho$ represents the active surface area per unit volume, and $K = k_a/k_d$ is the adsorption equilibrium constant, whose temperature dependence is given by

$$K = A \exp(U/RT), \qquad (2)$$

where U is the heat of adsorption. Notice that according to Eq. (1) the effective desorption rate constant

$$k_{eff} = \pi^2 D/\alpha\rho R_p^2 K \qquad (3)$$

depends on the size of the catalyst particle, i.e., on R_p. Likewise, the equation for the peak temperature, T_M, becomes (2)

$$(U\beta/RT_M^2) = (\pi^2 D/\alpha\rho R_p^2 A)$$
$$\exp(-U/RT_M), \qquad (4)$$

β being the heating rate of a linear heating schedule. Equation (4) shows that also the peak temperature is a function of the catalyst particle radius in a diffusional regime. We will now discuss briefly such dependences on a more quantitative basis.

(a) Changes in the peak temperature. Equation (4) supplies an implicit relationship between T_M and R_p. For (U/RT_M) ranging between 17 and 33, $10 \leq U \leq 40$ kcal/mol, and $\beta = 0.17$ K/s, Eq. (4) is well approximated by the expression

$$\Delta T_M = 3.7U \log_{10}(R_{p1}/R_{p2}). \qquad (5)$$

Equation (5) yields the expected variation of the peak temperature as an explicit function of the particle size. According to Eq. (5) such variations are not dramatic, but can be generally appreciated. For example, if $(R_{p1}/R_{p2}) = 1.5$, and $U = 20$ kcal/mol, the expected ΔT_M is about 13 K.

(b) Changes in k_{eff} at fixed temperature. From Eq. (1),

$$(k_{eff,1}/k_{eff,2})_T = (R_{p2}/R_{p1})^2. \qquad (6)$$

Along the lines illustrated in Refs. (4, 5) k_{eff} can be conveniently estimated from the experimental TPD curve as

$$(k_{eff})_T = \frac{\beta}{\tilde{S}} (C/\bar{\theta})_T, \qquad (7)$$

where $\tilde{S} = \int_0^\infty C \, dT$ represents the area underlying the TPD curve, while

$$\bar{\theta}_T = 1 - \frac{1}{\tilde{S}} \int_0^T C \, dT. \qquad (8)$$

Equations (5) and (6) provide the basis for experimental criteria determining whether significant internal mass transfer effects are present during TPD. Suppose that a few experiments have been run using particles of different sizes, all the other conditions being constant (namely the catalyst mass W_c and the carrier gas flow rate Q). If the experimental values for T_M and $\log_{10}(k_{eff})_T$ are plotted versus $\log_{10}(R_p)$, such plots should result flat when diffusional effects are negligible, whereas straight lines with slopes of approximately (3.7 U) and (-2) are expected where the limiting condition of rate-controlling pore diffusion with equilibrated readsorption is approached. In the following we demonstrate the application of these criteria to our data for TPD of methanol from a bed of γ-Al_2O_3 catalyst particles.

RESULTS AND DISCUSSION

Details about our experimental setup for TPD are given elsewhere (6). Table 1 reports the relevant catalyst parameters together with typical operating conditions. Figure 1 shows one of the spectra recorded during TPD runs. Gas-chromatographic

TABLE 1

Catalyst Parameters and TPD Operating Conditions

Average particle radius, R_p	$3.5 \times 10^{-3} \div 0.15$ cm
Surface area, α	1.7×10^6 cm^2/g
Catalyst density, ρ	1.06 g/cm^2
Mean pore radius, r_p	6.2×10^{-7} cm
Porosity, ε	0.56
Mass of catalyst bed, W_c	0.03 g
Carrier gas flow rate, $Q°$	2.5 cm^3/s
Heating rate, β	0.17 K/s
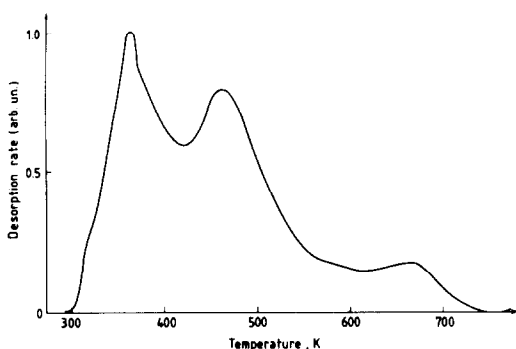
FIG. 1. Experimental TPD curve of CH_3OH from γ-Al_2O_3 · R_p = 3.5 × 10^{-3} cm (200–230 mesh). Q^0 = 2.5 cm³/s. W_c = 0.03 g.

analysis always detected only methanol as desorbed species; only small traces of dimethyl ether were observed in the temperature range 450–550 K. The articulate shape of the curve originates from the superposition of desorption peaks corresponding to diverse adsorption states. Among these, the first peak (T_M ≅ 360 K) is associated with a liquid-like physisorbed methanol species, and is representative of a homogeneous interaction between methanol and the catalyst surface. Assuming a symmetric shape for the first peak, and applying to it a single-curve, normalized treatment for the analysis of TPD spectra (4, 5), we estimate a heat of adsorption (U ≅ 9.7 kcal/mol) which compares with the heat of vaporization of methanol. Desorption peaks at higher temperatures are associated with several different chemical interactions between methanol and γ-Al_2O_3. Since the resolution of the TPD curve into its compo-

nent peaks is uncertain, however, we have chosen to refer only to the first peak of each TPD curve in the following discussion.

In Fig. 2 the temperature of the first peak maximum of the TPD spectra is plotted against R_p. Each point represents the average of a few replicated runs; also, the confidence limits of the measurements are shown. Though there is some scatter in the individual measurements, the trend of the data appears well defined. As the particle size is increased, T_M is first unaffected, then begins to grow, and finally a roughly linear dependence is approached. Figure 3 shows a plot of the observed desorption rate constant, k_{eff}, versus R_p. k_{eff} has been calculated from the TPD curves via Eq. (7) for two temperatures, 333 and 343 K. Again, no effect of R_p is noticeable in Fig. 3 as long as the size of the particles is sufficiently small. For bigger particles, increasing R_p brings about a reduction of the effective rate constant for desorption, as expected from Eq. (3). For both Figs. 2 and 3, the slopes of the plots in the region where the effect of R_p is apparent seem slightly smaller than the theoretical values predicted by Eqs. (5) and (6), respectively. This is likely due to the fact that full readsorption equilibrium is not yet achieved in our experimental conditions, as suggested by the small value of the readsorption rate constant k_a estimated from independent measurements. For each TPD run we have also estimated the heat of adsorption by the methods described in Refs. (4, 5). No significant effect of the particle size is appar-
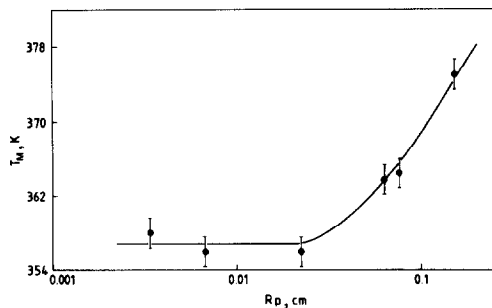

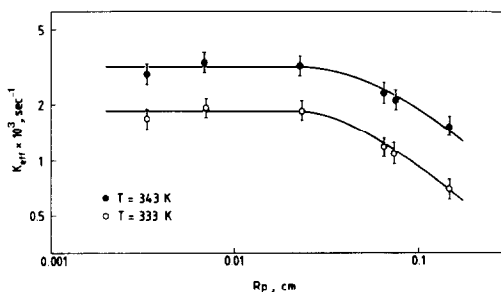FIG. 2. Effect of particle size on T_M, temperature of the first peak maximum.

FIG. 3. Effect of particle size on the effective desorption rate constant.
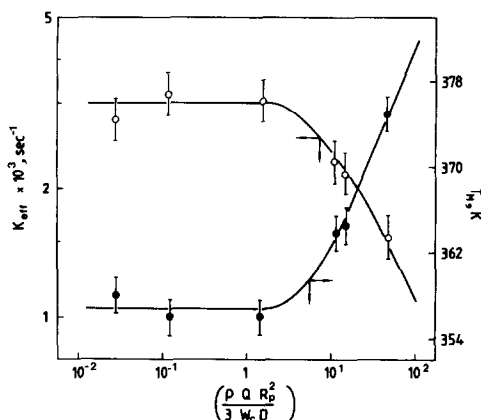
FIG. 4. Plot of k_{eff} at 343 K (open circles) and T_M (full circles) versus $(\rho QR_p^2/3W_cD)$, for comparison with Gorte's criterion (2).

ent in this case, so that the R_p dependence of k_{eff} shown in Fig. 3 is entirely due to its preexponential factor, as expected from Eq. (3).

The data for T_M and k_{eff} at 343 K have been replotted in Fig. 4 against the group $(\rho QR_p^2/3W_cD)$, which is equivalent to Gorte's group (Ql/DS) for a bed of spherical catalyst particles (3). Knudsen diffusion has been assumed to govern mass transfer in the pores; accordingly, the effective diffusivity has been estimated as (3)

$$D = \tfrac{2}{3}(8RT/\pi M)^{0.5}r_p\varepsilon^2, \qquad (9)$$

where M is the molecular weight of methanol. The carrier gas flow rate in the cell has been calculated from the value at room temperature $Q°$ as

$$Q = Q°(T/298). \qquad (10)$$

Notice that the only true variable in the abscissa of Fig. 4 is R_p, since both $Q°$ and W_c were kept constant during our experiments. The effects of the particle size are negligible for $(\rho QR_p^2/3W_cD) < 1$, in agreement with Gorte's theoretical considerations (2). On the other hand, the onset of strong diffusional effects occurs where $(\rho QR_p^2/3W_cD) \gg 1$. Therefore, the use of Gorte's criterion to evaluate a priori internal mass transfer limitations appears sound on the basis of the results obtained from our experimental system.

CONCLUSIONS

(1) This study demonstrates that it is possible to run TPD experiments using beds of porous catalyst particles with high surface area avoiding intraparticle diffusional limitations. Thus, it is confirmed that in principle the TPD technique can provide quantitative chemical information on the desorption process from porous catalysts.

(2) Changes in the temperature of the peak maximum and in the measured desorption rate constant as functions of R_p provide experimental criteria to detect the presence of intraparticle diffusional intrusions during TPD experiments.

(3) Such criteria have resulted in agreement with the a priori criterion already proposed in the literature.

(4) Both the observed changes of T_M and k_{eff}, and the observation that the variation of k_{eff} with R_p is due to a change of the preexponential factor only, are consistent with published theoretical treatments.

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ENRICO TRONCONI
PIO FORZATTI[1]

Dipartimento di Chimica Industriale
ed Ingegneria Chimica del Politecnico
Piazza Leonardo da Vinci, 32
I-20133 Milan, Italy

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[1] To whom correspondence should be addressed.