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Experimental Errors in the Application of Temperature-Programmed Desorption to Practical Catalysts

Temperature-programmed desorption (TPD) is a widely used technique for obtaining information on the nature of the interaction between adsorbed species and a surface (*1–4*). Many types of desorption processes are known (as surface reaction or migration being rate limiting) (*3–6*) which can lead to a variety of kinetic expressions for desorption. However, when studying the desorption of gases (which are nondissociatively adsorbed) from practical catalysts (having a high surface area, porous, refractory support) it is common to apply the mathematical formalism appropriate to first-order desorption:

$$2 \ln T_m - \ln \beta = E_d/(RT_m) + \ln (E_d/(AR)), \quad (1)$$

where T_m is the temperature of the peak maximum, β is the heating rate, E_d is the activation energy for desorption, R is the gas constant, and A is the preexponential factor (*1*). It is the purpose of this note to point out that such classically applied TPD is very sensitive to seemingly minor experimental errors and it is very difficult to obtain reliable kinetic parameters when applied to most practical catalysts even if the conditions required for the application of Eq. (1) are satisfied. An improved technique is suggested which is not sensitive to these errors, is more accurate, and is more sensitive than classical TPD.

The desorption of a molecule from a surface is a unimolecular decomposition: The adsorbed molecule decomposes into surface site plus free gas molecule. It is well known that the preexponential factor for a unimolecular reaction is given by

$$A = (kT/h)(Q^*/Q) \gtrsim 10^{13}\ \mathrm{s}^{-1}, \quad (2)$$

where k is Boltzmann's constant, T is the temperature, h is Planck's constant, Q is the partition function for the reactant system, and Q^* is the partition function for the transition state (*7*). Usually $Q^*/Q > 1$ because the transition state normally reflects the increase in the degrees of freedom (higher entropy) of the products. For gas-phase unimolecular decompositions, most values of Q^*/Q fall in the range of 1 to 1000 (*7*). Preexponential factors have also been reported for the desorption of gases from metal filaments and single crystals and where it is believed that a first-order process is rate limiting there is again reasonable agreement with theory (*5, 8–15*).

The application of TPD to practical catalysts usually results in frequency factors which are many orders of magnitude lower than predicted by Eq. (2) (*16–23*); values as low as 10 s^{-1} have been reported (*16*). Particularly enigmatic are the results for a series of olefins desorbed from γ-alumina (Table 1). Although ethylene yields a normal value for A, its homologs yield anomalously low values and the value of E_d *decreases* as the molecular weight and boiling point of the olefins

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TABLE 1

Kinetic Parameters for the Desorption of Olefins from Alumina

Olefin	TPD technique		Ref.	Semiempirical technique	
	E_d (kcal/mol)	A (s^{-1})		E_d (kcal/mol)	A (s^{-1})
Ethylene	26.8	2×10^{15}	(*24*)	24.7	7×10^{13}
Propylene	14.2	7×10^{5}	(*17*)	28.5	8×10^{13}
trans-2-Butene	12.1	1×10^{4}	(*18*)	30.7	9×10^{13}

increase. It appears, then, that the application of TPD to such systems may be unreliable (high flow rates were used to minimize readsorption in these experiments).

Errors in the value measured for T_m due to the nonzero response time, τ (the time to reach 63% of the final value when subjected to a step change in temperature), of the thermocouple used to monitor catalyst temperature can seriously affect the data derived by application of Eq. (1). It is common practice to encase the thermocouple in a glass well (*1*) and an equation can be derived showing that this will cause the measured temperature to lag behind the true temperature of the catalyst by the amount

$$\Delta T = \beta\tau.^1 \qquad (3)$$

For a typical configuration of a 20-gauge thermocouple in a 6-mm-o.d. Pyrex sheath, τ is about 0.5 min for immersion in a bed of silica. For β ranging from 5 to 30 K/min, this will cause temperature errors of 2.5 to 15 K in the value of T_m. Although this can have a dramatic effect on the kinetic parameters derived for practical catalysts (Fig. 1), only rarely has the possibility of thermocouple lag been considered and we are not aware of any quantitative evaluation of the effect.

Any process which delays the detection of gas after it has been desorbed will shift T_m to higher values and counteract the effect of thermocouple lag. Likely candidates include inaccurate correction for the dead time between reactor and detector and diffusional delays. Means of estimating average diffusional times are well known and the amount of delay depends on the effective diffusivity and distance into the catalyst particle at which the gas is desorbed. Diffusivities span a range from about 0.1 to 10^{-10} cm^2/s, and for the lower values (as is characteristic of zeolites) diffusion, rather than desorption, can be the rate-limiting step for the appearance of gas during TPD (*25*). Although the statistical nature of diffusion clearly precludes assigning an exact value for a delay, nonetheless the error will again increase linearly with β and it is of heuristic value to compare the effects of a 0.5-min system delay and thermocouple lag (Fig. 1). It is clear that very small errors in measuring T_m (including the intrinsic difficulties of making highly accurate temperature measurements on a nonisothermal system) can substantially affect the kinetic parameters derived from Eq. (1), even assuming the equation is applicable to the system being studied.

We have reduced errors due to thermocouple lag to an insignificant level by using a bare, 30-gauge thermocouple immersed in the catalyst bed to measure catalyst temperature (a separate thermocouple, external to the reactor, is used to sense the power requirement for the oven). Alternately, if the possibility of contamination exists, the thermocouple can be encased in a thin piece of glass which is blown out

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[1] ΔT is actually the steady state error, which will be reached in a time of $\sim 3\tau$.

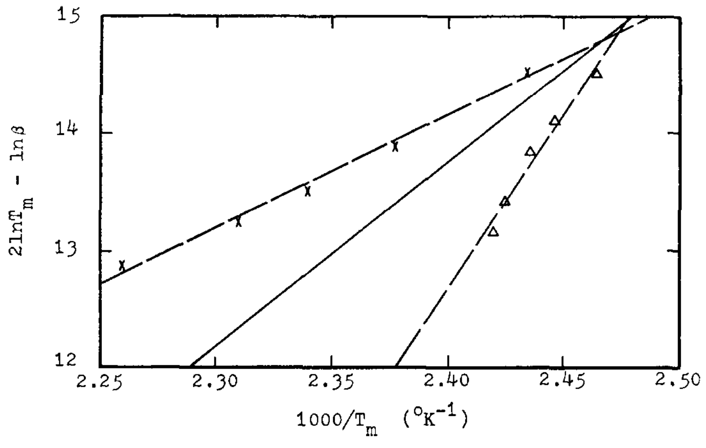

FIG. 1. Effect of thermocouple lag and system delay on kinetic parameters derived from TPD. (——) Ideal data for E_d = 30 kcal/mol and $A = 10\ kT_m/h$. (△) Experimental data assuming the thermocouple response time (τ) is 0.5 min. This line yields E_d = 59.0 kcal/mol and $A = 8 \times 10^{29}\ s^{-1}$. (X) Experimental data assuming the system delay is 0.5 min. This line yields E_d = 19.0 kcal/mol and $A = 6 \times 10^7\ s^{-1}$.

and collapsed around the tip of the thermocouple. The former arrangement has a response time of 0.033 min, and the latter, 0.1 min. The small residual error is removed by application of Eq. (3).

The cases of the effect of pore structure on peak shape under isothermal conditions (reversible desorption also occurring) (*26*) and during TPD (diffusion rate limiting) (*25*) have been mathematically treated. However, even in these limiting cases the mathematics is complex and the effort seems to transcend the usefulness of TPD. We have found it easier to develop a complementary method for obtaining the kinetic information associated with TPD peaks.

Kinetic parameters can be obtained by making isothermal measurements of the rates of desorption over a small temperature range and applying the Arrhenius equation. By waiting for the steady-state response of the detector at each temperature, errors due to thermocouple lag or system delays are eliminated. However, one does not know at what temperature the experiments should be performed and the surface becomes depleted of adsorbed species during the experiments, making interpretation difficult. These problems can be overcome by using the integrated, isothermal, initial Slope (IIIS) technique which combines the more attractive features of TPD with isothermal measurements. A preliminary TPD run is done with $\beta \cong 5$ K/min to locate the peak of interest. The rate of desorption is now measured isothermally at temperatures limited to the initial slope (leading edge) of the desorption peak. Sensitivity is enhanced about 20-fold by trapping the effluent from the reactor for about 1 min in a suitable adsorbent (like silica gel at −196°C) and releasing it as a sharp pluse by rapid heating, thus effectively integrating the signal over the time of trapping (a preliminary check without trapping quickly establishes the time required for the various transients to die out when the temperature of the catalyst is changed). It is possible to obtain the rates of desorption at five different temperatures while removing <5% of the adsorbate, thereby maintaining pseudo-zero-order kinetics.[2] This technique

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[2] If higher accuracy is desired the rate data can be corrected for the small changes in coverage by desorption at a high temperature to allow the calculation of the initial coverage.

TABLE 2

Comparison of Experimental Techniques for Obtaining Kinetic Parameters

Technique	E_d (kcal/mol)	A (s^{-1})
TPD	13.6	6×10^4
IIIS	33.3 ± 1.5^a	6×10^{15}
Semiempirical	30.6 ± 1.5^a	9×10^{13}

[a] Mean ± SD.

not only is immune to the errors which so severely affect standard TPD, but is also about 100-fold more sensitive and does not require an absolutely stable baseline over long periods.

The results of the standard TPD approach and the IIIS method are compared in Table 2 for the temperature-programmed decomposition of $Cr(CO)_6/SiO_2$. This system was chosen because the CO peak width at half-maximum is 24 K (only a single peak is observed), in excellent agreement with theory (23 K). Also, desorption of the CO is essentially irreversible (*27*), so it appears that the assumptions built into Eq. (1) are probably satisfied for this system. It is evident that TPD gives the usual low value for A (and therefore also low value for E_d; correction was made for dead time and thermocouple lag) whereas IIIS gives a reasonable and self-consistent value for A (and therefore reasonable value for E_d).

Where semiquantitative data are sufficient, these results also suggest that a semiempirical technique may be useful. In this approach it is assumed that $A = 10\ kT_m/h$, the factor of 10 being included as a reasonable estimate for Q^*/Q. With this assumption, a single experiment determines T_m and β which then implicitly determine E_d by Eq. (1). A table of T_m as a function of E_d and A/β is available (*2*). This was, in fact, the original method by which flash desorption data were analyzed (*28*), but has been rarely used in deference to more rigorous approaches. The main problem with this technique is the effect which uncertainties in the value assigned to A and in the measurement of T_m can have on the value computed for E_d. Application of Eq. (1) shows that each tenfold error (increase) in the value of A only increases E_d by 6% and each +1 K of error in T_m only raises E_d by 0.08 kcal/mol. Thus, the semiempirical technique is relatively insensitive to these errors and in cases where there is reason to believe that the desorption is first order this approach may be quite useful (Table 2).

In conclusion, we reiterate that, even for systems for which the desorption is first order, the application of Eq. (1) can easily yield erroneous values for the kinetic parameters due to the sensitivity of the equation to small experimental errors. There are, of course, other techniques for extracting the kinetic information (*3*, *4*, *29*), but they generally require unperturbed peak shapes and have rarely been applied to desorption from practical catalysts (*30*). The IIIS technique avoids these problems and also provides increased sensitivity by combining the better features of TPD with isothermal measurements.

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