Temperature-Programmed Desorption of Adsorbed Species from Catalyst Surfaces

1. Background

Temperature-programmed desorption (TPD) of species chemically adsorbed (chemisorbed) on the surface of metal oxides or supported metal catalysts is a technique commonly applied in the characterization of heterogeneous catalysts. TPD can provide information about surface acidity/basicity, reaction kinetics, metal dispersion, and reaction mechanisms.

For supported metal catalysts, the chemisorption uptake may be used to calculate an average metal crystallite size. This information provides a basis for comparing the performance of different catalysts. Different catalyst preparations may vary significantly in characteristics such as composition, density of the material or metal weight loading. The chemisorption characteristics of a catalyst may be more closely related to the catalyst's chemical activity than these other physical characteristics. Knowledge about sites for chemisorption may be used to develop catalytic rate expressions based on the number of adsorption sites rather than the gross catalyst weight or volume. Catalyst activity given on a per site basis makes comparison of the true efficiency of different catalysts more meaningful.

2. TPD Experimental Methods

A typical TPD experiment consists of several steps:

Pretreatment: The sample is first subjected to calcination, reduction, or out-gassing usually at elevated temperatures to remove water and impurities and to prepare the catalyst surface for the chemisorption step.

Chemisorption: The sample is contacted with the molecule of interest in one of several different modes, including pulse adsorption, steady flow adsorption, or static non-flow adsorption. The chemisorption process may be carried out to the extent that the surface is fully covered with adsorbing molecules or to some fraction of full coverage.

Desorption: After the surface has been contacted with the adsorbing molecule to achieve the desired coverage, the temperature of the system is raised in a linear fashion while a constant flow of an inert gas passing over the catalyst. Desorbing molecules leaving the catalyst surface are swept into this stream of inert gas and are carried to a detector which monitors the amount of gas and the temperature at which it desorbs. Desorption into this gas stream occurs when an adsorbed species gains enough energy to overcome the activation energy barrier to the desorption process.

3. Interpreting TPD Results

TPD experimental results are presented as a plot of detector signal intensity (which can be calibrated to give its relationship to the amount of gas desorbing) versus sample temperature, as shown in Figure 1. A TPD plot can provide information about the number of surface sites exposed and available for chemisorption of a molecule of interest. The number of adsorbed molecules is found simply by integrating the area under the desorption curve. Chemical properties of the chemisorption sites can also be investigated by TPD. Generally, molecules that are weakly bound to the surface desorb at lower temperatures, and those strongly bound to the surface require higher temperatures to desorb. This is modelled in Figure 1, showing two representative peaks for a weakly bound adsorbate (Peak A) and a strongly bound adsorbate (Peak B). The relative quantity of each species can be determined by integrating the area under each peak.

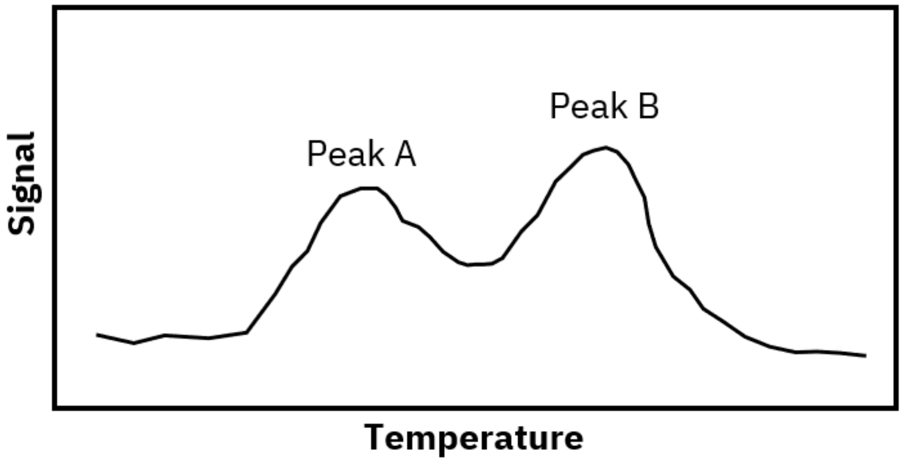

Figure 1: Representative TPD plot showing the intensity of the desorbed molecule signal as a function of temperature. A weakly adsorbing species is shown as Peak A, and a strongly adsorbing species is shown as Peak B.

3.1 Relating Kinetic Information to TPD Results

In addition to providing a quantitative measurement of gas uptake by a catalyst surface, TPD experimental results also contain information about kinetic parameters of the adsorption-desorption processes on the catalyst surface. These parameters may be obtained from the known quantities of inert gas flow rate, linear heating rate and desorption peak temperatures.

Several papers have discussed the equations which describe the desorption of molecules from catalyst surfaces.(1-3) These equations give rate constants and activation energies, as well as the order of the desorption process. Comparison of these parameters for a series of catalysts may delineate trends which help to explain observed differences in catalyst performance. Caution must be taken, however, in utilizing this kinetic information because, as described below, heterogeneous catalyst systems often present experimental complications not addressed in kinetic treatments developed for simpler cases.

4. Effect of Variables on TPD Experiments

One important feature of TPD that should be kept in mind is the transient nature of the experiment. Three variables change continuously over the time of the experiment:

- ✓ Temperature
- ✓ Surface coverage of the adsorbate
- ✓ Desorption rate

These variables are plotted qualitatively in Figure 2 (redrawn from reference 3). The implication is that a TPD experiment is always performed under changing conditions which may be far removed from reaction conditions under which the catalyst is likely to be used. Thus, it is quite important to understand how to interpret TPD spectra so that proper relationships between desorption characteristics and activity of a catalyst may be established.

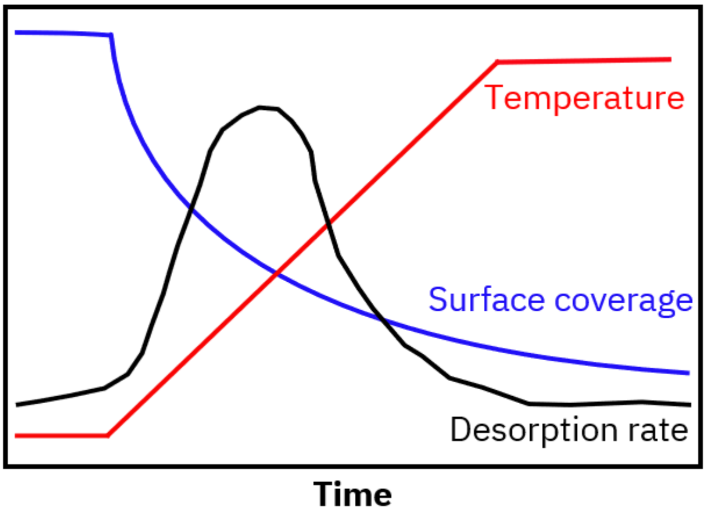

Figure 2: Plot showing the relationship between TPD variables as a function of time: temperature (red), adsorbate surface coverage surface coverage (blue), and adsorbate desorption rate (black).

4.1. Heating Rate and T$_{des}$

Changing the linear temperature ramp rate for desorption causes the temperature of desorption (T$_{des}$) to change, as shown in Figure 3. This relationship is described in the Redhead equation (Eqn. 1); higher heating rates increase the temperature of desorption. Additionally, species re-adsorption adds a time increment to the normal time it takes for a desorbing molecule to reach the detector, which is not accounted for in the Redhead equation. For example, consider a sample which adds a time increment of 180 seconds due to re-adsorption after the initial desorption of a molecule at 100 °C. Molecules arriving at the detector are marked at erroneous temperatures, as shown in Table 1.

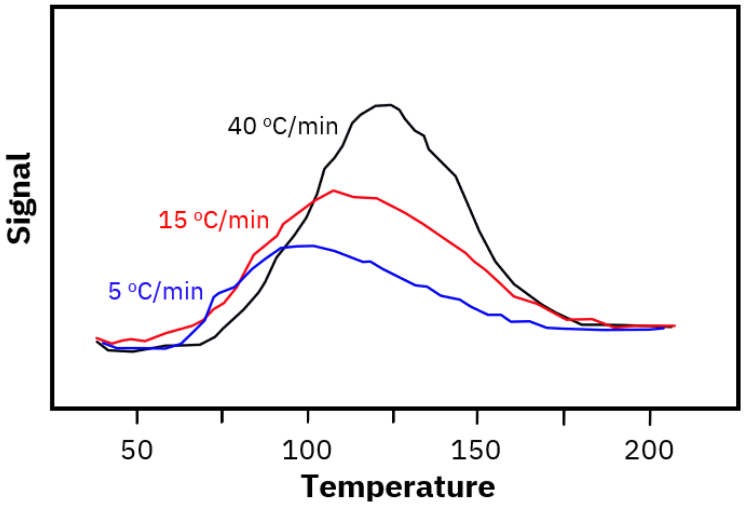

Figure 3: Representative TPD plot showing the effect of heating rate on measured desorption peak temperature.

$$\frac{E_{des}}{RT_{des}} = ln\left(\frac{\nu T_{des}}{\beta}\right) - 3.64 \qquad \text{Eqn. 1}$$

Heading rate (°C/min)	Detected T_{des} (true T_{des} = 100 °C)
5	115
10	130
20	160
30	190
40	220

Table 1: Heating rates and the resulting erroneous desorption temperatures for a sample with an added 180 seconds to reach the detector (due to re-adsorption).

In which:
E_{des} = desorption energy
T_{des} = desorption temperature
ν = pre-exponential factor, typically assumed to be $10^{13}\ s^{-1}$
β = heating rate
R = gas constant

4.2. Gas Flow Rate and T_{des}

The flow rate of inert gas over the catalyst surface during TPD will also influence TPD curves. Higher flow rates carry desorbed molecules to the detector more quickly and hence minimize the time lag between the actual desorption temperature and the detected desorption temperature. For example, suppose that the experiment with the catalyst sample described above was carried out with an inert gas flow rate of 25 mL/min in a tubular sample cell with 10 mL volume between the catalyst bed and the detector. Increasing the flow rate to 200 mL/min cuts the total time lag from 180 sec to 161 sec. For a ramp rate of 20 °C per minute, the difference between the true and detected desorption temperatures decreases from 160 to 153°C.

4.3. Sample Porosity and T_{des}

Quantitative treatment of desorption kinetics has been developed for the case of desorption from homogeneous, nonporous surfaces as well as for the more complicated cases which can arise for porous heterogeneous catalysts.(3-5) One of the most important of these complications is that species desorbing from porous surfaces may be held up as they diffuse through the catalyst pores by re-adsorbing on sites along the molecule's pathway in the pore.

Desorption from homogeneous, flat samples such as single crystals of metals results in "flash

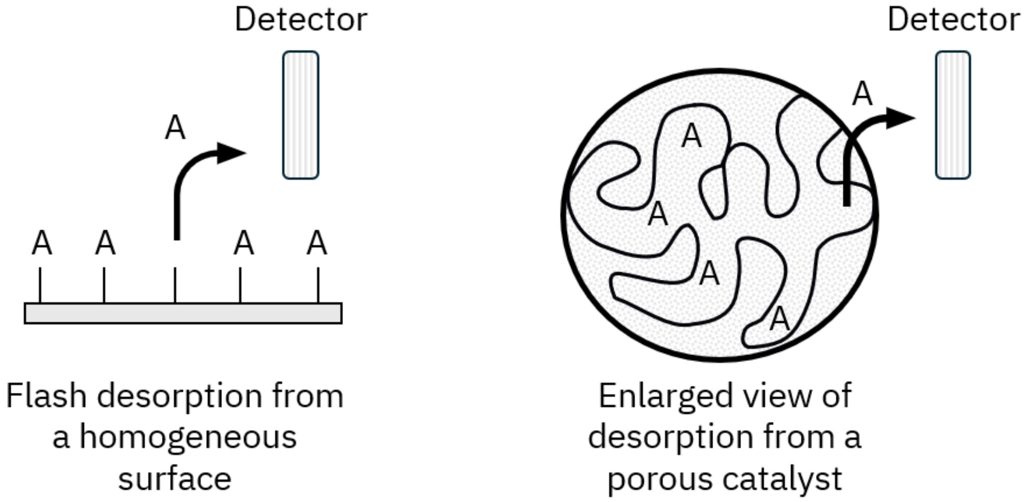

Figure 4: Diagram comparing the geometrical differences between species A desorbing from a homogeneous flat surface (left) and porous sample (right).

desorption" in which there is very little holdup between the surface and the detector.
Desorption from porous samples, however, can be followed by slow diffusion through pores and even re-adsorption onto other surface sites. This wandering path of the desorbing molecules causes them to arrive at the detector much later, as shown in Figure 4.

4.4. Minimizing Gas Re-adsorption

The above examples show that decreasing the ramp rate and increasing the inert gas flow rate both help to close the gap between true and detected desorption temperatures.

Increasing the flow rate can certainly minimize the lag time between the end of the sample bed and the detector, but it has little effect on the residence time of desorbing molecules within the catalyst bed itself. Internal diffusion rates in catalyst micropores are not affected by changes in the flow rate of gas outside the pore. In addition, the time lag is due not only to diffusion of the desorbing gas but also due to its re-adsorption on sites within the catalyst pores. The adsorption residence time on catalyst surface sites is not affected by external gas flow rate.

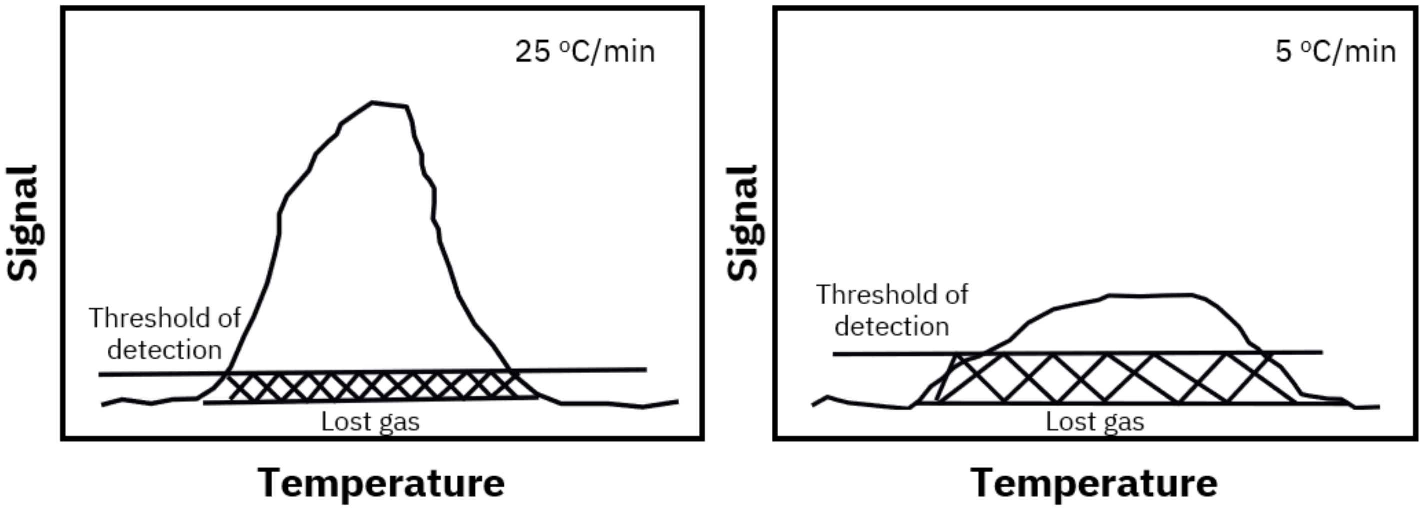

Figure 5: TPD plots comparing the fractions of desorbed gas "lost" below the instrument threshold of detection at heating rates of 25 °C/min (left) and 5 °C/min (right).

Decreasing the temperature ramp rate can lessen the temperature lag between true and detected desorption temperature, but it can also change features of the desorption curves. A desorption trace recorded at a slower ramp rate appears to be "flattened". For molecules adsorbed on a heterogeneous surface, a wide spectrum of energies of desorption can exist. At slower ramp rates, desorption is spread out over longer time. Some amount of desorbing gas below the detector's "threshold" is always undetected due to experimental constraints, and the slower desorption occurring at slower ramp rates results in a larger fraction of the gas being "lost" below the threshold detection limit, as shown in Figure 5.

While changes in the experimental conditions can't negate all the problems inherent in studying desorption from heterogeneous surfaces, there is quite a lot to be learned by trying different flow rates and ramp rates for TPD experiments over any given catalyst. Investigating the desorption spectra for a variety of conditions can often help to develop a standard experimental technique to be used for a whole series of catalysts. This method of "fingerprinting" catalysts is a useful means of recording trends in adsorption and desorption to compare with trends in catalyst performance.

5. References

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