Temperature Programmed Desorption

Normally any kinetic study involves the monitoring the concentration of an y one of the species in the reaction as a function of both mostly time and also sometimes temperature. However, in the Temperature Programmed techniques (TPX)since time and temperature are interrelated by the expression $T(t) = T_0 + \alpha t$ (where T is the temperature at any time t, T_0 is the start temperature and α is the heating rate that is (dT/dt) in the units of K/sec), it provides a means to study two variables of a reaction at the same time, this method has attracted considerable attention.

There are a range of techniques for studying surface reactions based on temperature sweep. Molecular adsorption on surfaces can be studied using temperature-programming to discriminate between processes with different activation parameters. Temperature programmed techniques can be reduction, oxidation, reaction, sulphdation, and hence there can be a number of TPX techniques where X stands for the process that is being studied. Experimentally too, this method of analysis is simple requiring a simple pressure gauge or a chemical analytical tool like gas chromatograph or a mass spectrometer. Even a pressure measurement as a function of time and temperature may be sufficient in some instances. The basic experiment is very simple, involving the following two steps in the case of desorption

1. Adsorption of one or more molecular species onto the sample surface at low temperature (frequently 300 K, but sometimes sub-ambient).
2. Heating of the sample in a controlled manner (preferably so as to give a linear temperature ramp) while monitoring the evolution of species from the surface back into the gas phase.

The data obtained from such an experiment consists of the intensity variation (the concentration of the desorbed species) of each recorded mass fragment as a function of time / temperature. In the case of a simple reversible adsorption process it may only be necessary to record one signal - that is attributable to the molecular ion of the adsorbate concerned. Typical TPD trace for the desorption of CO adsorbed on Pd (111) at 300 K is shown   in   Fig.1.
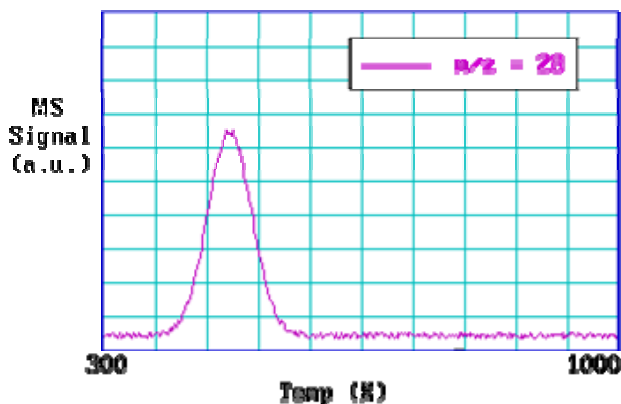
Fig.1. Typical TPD trace for adsorbed CO on Pd (111) at 300 K.

Since mass spectrometric detection is used normally the sensitivity of the technique is good with attainable detection limits below 0.1% of a monolayer of adsorbate.

The following points are worth noting:

1. The area under a peak is proportional to the amount originally adsorbed, i.e. proportional to the surface coverage.
2. The kinetics of desorption (obtained from the peak profile and the coverage dependence of the desorption characteristics) give information on the state of aggregation of the adsorbed species e.g. molecular or dissociative adsorption.
3. The position of the peak (the peak temperature) is related to the enthalpy of adsorption, i.e. to the strength of binding to the surface.

If there is more than one binding state for a molecule on a given surface (and if these have significantly different adsorption enthalpies) then one will be able to discriminate them from the multiple peaks in the TPD spectrum.

Theory of TPX Techniques

The rate of desorption of a surface species will in general be given by an expression of the type

$$R_{des} = \nu\, N^x \exp(-E_a^{des}/RT)$$

where R_{des} is the desorption rate (= - dN/dt), x is the kinetic order of the desorption and E_d^{des} is the activation energy for desorption.

In a temperature programmed desorption experiment since as stated above the temperature and time are related by the expression

$$T = T_0 + \alpha.t \quad \text{and} \quad dT = \alpha.dt,$$

where T_0 is the starting temperature .

The intensity of the desorption signal, $I\,(T)$, is proportional to the rate at which the surface concentration of adsorbed species is decreasing. This can be expressed as

$$I(T) \ \alpha \ \ dN/dT \ = \ (\nu N^x /\alpha) \exp (-E_a^{des}/RT)$$

This problem can also be understood in terms of some graphical representation.   The equation for signal intensity consists of two terms corresponding to the surface coverage and the exponential term.   At low temperatures, the exponential term is small and it increases with increase of temperature and the increase is significant when the value of RT is equal to E_a.

On the other hand, the coverage dependent term remains constant initially and decreases rapidly as the desorption temperature is approaching and attains the value of zero at some temperature. The graphical representation of the variations in the pre-exponential term and the exponential terms is given in Fig.2. The shaded area can be considered as the desorption trace. The description given is a very simplistic one but it will be suffice to understand the origin and shape of the desorption trace.

Fig.2. The variation of the pre-exponential term and the exponential term as a function of temperature. The shaded area represents the desorption trace.

Let us consider a simple case for understanding the nature of desorption traces one will obtain. The case that is considered is (i) adsorption is as a molecular species and (ii) the order of desorption is unity..

The maximum in the desorption trace (that is the signal $I(T)$ will attain a maximum value) will occur when $(dI/dT) = 0$,

i.e. when

$$(d/dT)[(vN/\alpha) \exp(-E_a^{des}/RT)\} = 0$$

Which can be rewritten taking into account that surface coverage N itself is a function of temperature

$$(vN/\alpha).(E_a^{des}/RT) \exp(-E_a^{des}/RT) + (v/\alpha) \exp(-E_a^{des}/RT). dN/dT = 0$$

Substituting for dN/dT, one gets

$$(vN/\alpha)[(E_a^{des}/RT) - (v/\alpha) \exp(-E_a^{des}/RT)]\exp(-E_a^{des}/RT) = 0$$

The solution is given by setting the expression in square brackets to be equal to zero,

i.e. $E_a^{des}/RT_p^2 = (v/\alpha) \exp(-E_a^{dea}/RT_p)$,

where T_p represents the peak maximum temperature. One can notice that :

1. Depending on the value of E_a^{des} the peak maximum temperature also varies, higher the value of E_a^{des} higher will be the peak temperature T_p.
2. The peak maximum temperature is independent of the initial coverage.
3. The shape of the trace will depend on the rate of desorption process and it will decrease rapidly after the desorption maximum.

More detailed quantitative information on TPD is beyond the scope of this book and they can be found elsewhere.

In general this technique can provide a variety of information on various aspects of adsorption and catalysis. They are:

1. Mechanistic aspects of reaction under study (the technique in this case is referred as Temperature Programmed Reaction Spectroscopy TPRS)
2. Identification of the nature of active sites, binding states of adsorbed species binding energy of the adsorbed species.
3. The influence of preparation procedures on the catalysts developed
4. Effects of active phase, chemical composition, promoters dispersion, surface groups
5. Active phase support interaction, alloy/compound formation

In this section, only a very simple cases of desorption spectra are shown as examples for the study of the surfaces from the list given.   Details on other specific applications can be found in literature.

Binding state of adsorbed species:

It is often known that the adsorbed molecules can have more than one mode of adsorption.   A simple molecule like hydrogen can also be adsorbed in more than one state.   These states are often identified from the temperature at which desorption takes place. A simple case is the adsorption of CO on top site, in a two fold site and multi-fold site depending on coverage and other reaction conditions. The desorption trace of CO from W is shown in Fig,3 together with the flash desorption curves obtained for the same systems.   It can be easily recognized that three adsorbed states of CO are discernable in both the thermal desorption and flash desorption traces indicating that CO is adsorbed on W surfaces in three different forms.   It is therefore possible to identify the multiple binding states of the adsorbed species and also the binding state that is responsible for a given surface transformation can also be recognized.
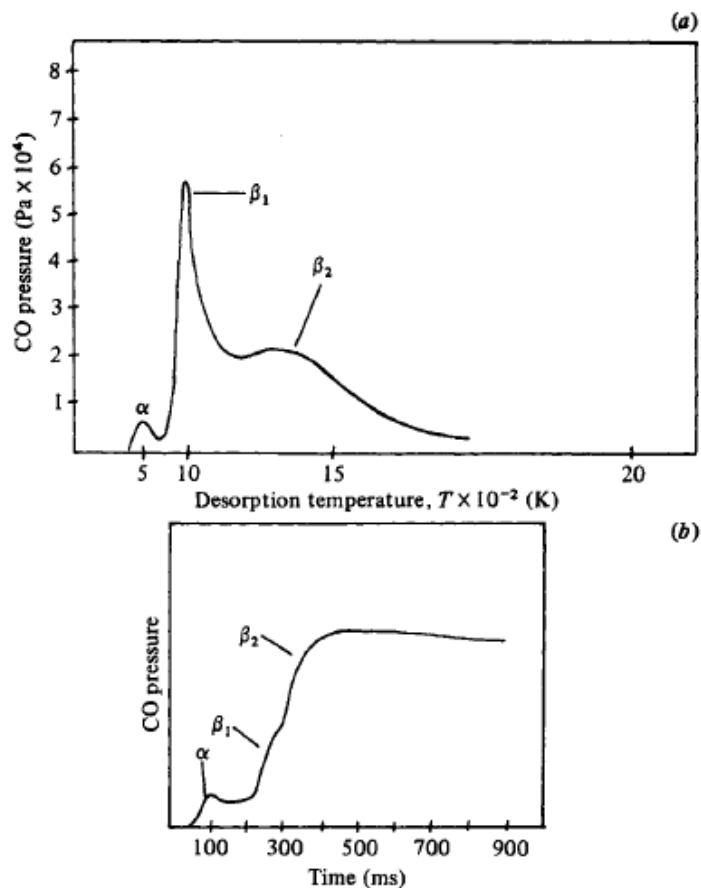
 Fig .3. (a) Thermal desorption trace and (b) flash desorption curve for the desorption of CO from W surfaces. It can be seen that there are three distinct adsorption states denoted by α, $β_1$ and $β_2$ states.

As stated above even for simple molecules like hydrogen more than one desorption peak can be observed.   Even though one may not be able to visualize more than one adsorption statein some cases, the repulsive interactions among the adsorbed molecules as function of coverage can result in multiple peaks in traces of desorption profiles. One such example for hydrogen adsorption on W is shown in Fig. 4.
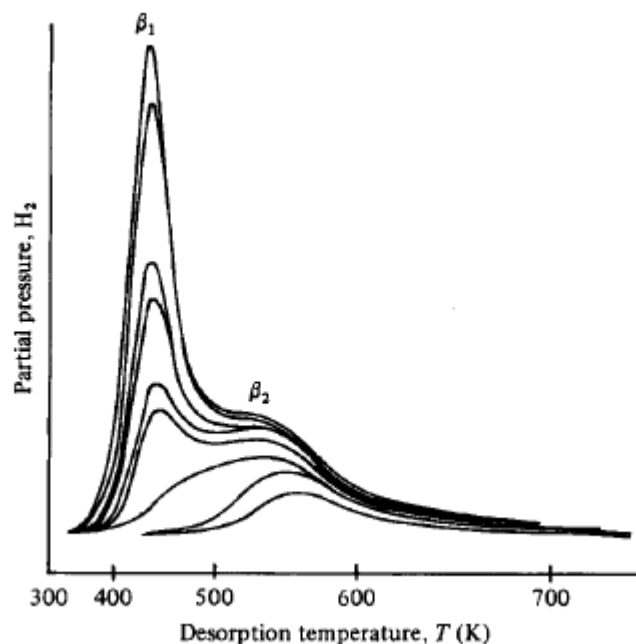
Fig.4.Thermal desorption trace for hydrogen from W (100) showing β_1 and β_2 state and it is seen that β_1 state is seen only when the coverage increases. The different curves correspond to desorption at various initial coverage of hydrogen on W (100).

TPD is one of the widely used techniques for characterizing the acid sites of most of the catalyst surfaces. The number and strength of acid sites on surfaces of alumina, silica-alumina and zeolties have been found necessary for understanding the surface transformations like n-hexane cracking, xylene isomerization, propylene polymerization, methanol-to-olefins reaction, toluene disproportionation, and cumene cracking that take place on these surfaces. In all these reactions, it is often recognized that the Bronsted acid site density is a crucial factor.

Conventionally there are three types of molecular probes commonly used for characterizing acid sites using TPD: They are (i) Base molecules like ammonia, pyridine or other amines (ii) Non-reactive vapours and (iii) Reactive vapours.

Even though, conventionally TPD of ammonia is employed to monitor the acidity of the solids, the values obtained are always higher since ammonia, being a small molecule can access almost all the pores of the catalysts while typical reactant molecules may not be able to access all the pores of the catalysts. In addition since ammonia is a basic molecule it can titrate all the weak acid sites but these weak acid sites may not be promoting the typical reactions considered. These points must be kept in mind while interpreting TPD of ammonia as a measure of the acidity of the porous solids as well as correlating the acidity with the observed catalytic activity.

Larger non-reactive amines such as pyridine and t-butyl amine are often preferred alternatives to ammonia because their sizes permit access to the pore size range required

for catalytic cracking and other reactions and they also titrate only the strong and moderate acid sites. The most common application for these probes is the characterization of pyridine adsorption by infrared spectroscopy where in both Bronsted acidity and also Lewis acidity are evaluated based on the absorption frequency. (can we give here typical values of the absorption frequencies)However, the determination of extinction coefficients is difficult and IR of pyridine is typically used in a qualitative manner, rather than as a measurement of site densities. While using aliphatic amines as probes for monitoring the acid sites and strength of solids, one has to exercise caution In Fig. 5, the TPD traces for the desorption of n-butylamine and n-propylamine from the surface of HY zeolite are shown. Though both amines show distinct desorption patterns, the on line mass spectral analysis of the desorption products showed the presence of butenes, higher olefines, dienes and aromatics. The observation is significant in veiw of the fact that alkyl amine uptake and it's desorption patterns are generally used for estimating the acidity of the catalysts. This observation of such desorption products even from weakly acidic NaY zeolites indicates that caution has be exercised to treat the TPD data of alkyl amines for the determination of acidity of solids. While using reactive probes like alkyl amines, the postulate is that the amines are protonated by the Bronsted acid sites to form the alkyl ammonium ions which can decompose to give rise to ammonia and olefins in a well defined temperature range proceeding proceeding like a Hoffman elimination reaction. If this were to take place then acidity of the solids can be monitored using alkyl amines.

TPD has also been used to determine the effect of catalyst precursors and also the type of interactions between the active precursor and the support. In Fig.6. temperature programmed reduction trace of Ni (OH)$_2$ prepared by urea hydrolysis is shown. It can be seen that the TPR profile shows a pattern with doublet peaks corresponding to the reduction of the rhombohedral and cubic forms of NiO. The controls are also shown in the same figure. In Figure.7. TPR patterns of hydroxide prepared by impregnation -of different nickel hydroxides are shown. Four different stages of NiO reduction characterized by bound states could be identified. They are free NiO in the rhombohedral and cubic forms, NiO getting reduced by an autocatalytic process, a bound state of NiO which gets reduced at higher temperature and another state of NiO which is irreducible. Thus it is seen that the finer details of the active phase support interactions are manifested in the TPR profiles. The quantitative data generated from these TPR profiles are given in Table 1 to substantiate the deductions made.

Table 1 Reduction behaviour of supported NiO precursors

Sample designation *	Free NiO weight percentage	Surface difficultly reducible	Bulk Spinel irreducible percentage	Total reducibility %
EAL(a)	7.26	48.74	44.0	56
EAE(b)	7.00	64.00	29.0	71

EAA©	8.90	65.10	26.0	74
EEO(d)	18.60	71.54	14.0	86

* metal loading 30 weight percent Ni) and alumina support is the same. Ni deposition from a solution of nickel nitrate was carried out by different methods.(a) by urea hydrolysis (b)as Ni-hexammine complex (c) by addition of ammonia (d)by equilibrium adsorption from nickel nitrate. Temperature programmed reaction spectroscopy (TPRS) is also increasingly employed now a days. A simple example of formic acid decomposition on copper surface is considered. In TPRS a number of desorption products will normally be detected by one of the analytical techniques like mass spectrometry, gas chromatography or simple pressure measurement.
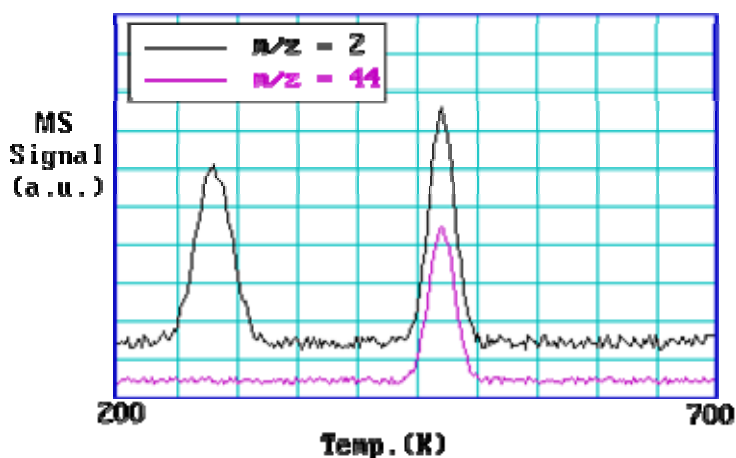
The desorption spectra shown in Fig.8. contain two regions - the first at around room temperature where there is desorption of hydrogen ($m/z = 2$) is observed and the second between 400 & 500 K where there are coincident desorption attributable to hydrogen and carbon dioxide ($m/z = 44$). The lower temperature hydrogen peak is at about the same temperature at which hydrogen atoms recombine and desorbs as molecular hydrogen from a hydrogen-dosed Cu (110) surface. The higher temperature hydrogen peak is observed well above the normal hydrogen desorption temperature - its appearance must be governed by the kinetics of decomposition of another surface species. The carbon dioxide peak must also be decomposition limited since on clean Cu (110) carbon dioxide itself is only weakly physisorbed at very low temperatures. Simultaneous desorption of carbon dioxide and hydrogen indicates the surface transformations of the adsorbed formic acid on the copper surface. Detailed mechanistic aspects of the surface transformations can also be elucidated from the various species that appear in the TPR traces.

There are various other aspects of the temperature programmed desorptin profiles that are not considered in this presentation. It is possible that multiple desorption peaks can overlap demanding a deconvulution of the trace to identify both qualitatively and quantitatively the nature of the desorbed species.

The peak shapes are usually identified by a factor called '*shape index*' which is the ratio of the two horizontal lengths drawn to the normal at the half height of the peak maximum. Any value other than 1 for this ratio indicates some complicating or simultaneous processes taking place during desorption. These manifestations can also be advantageously used to deduce details of the surface processes.

References:

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