

HIDEN CATLAB Microreactor – MS for Catalysis Studies



Catalyst characterisation, kinetic and thermodynamic measurements

- **TPD, TPO, TPR, TP-Reaction**
- **Catalyst Screening**
- **On-Line continuous product analysis**
- **Metal Surface Area**
- **Reaction Kinetics**
- **Mechanisms of Surface Reactions**
- **Heats of Adsorption and Co-adsorption**

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2. Catalyst Characterisation
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The CATLAB Microreactor – Mass Spectrometer

The HPR CATLAB microreactor module incorporates a fast response, low thermal mass furnace with Hiden's Catalyst Cartridge System for simple, reproducible sample placement with minimal changeover time. In addition the use of the Hiden close-coupled hot-zone evolved species probe directly coupled to the *QIC* inlet, provides for ultra-fast, high response sampling of desorbed species or evolved products. The HPR CATLAB microreactor is customisable to specific user requirements and may be configured for manual, semi-automatic or fully automatic operation, with standard gas manifold options comprising 2, 4, 6 or 8 gas streams with combined gas / vapour manifold and corrosion resistant manifold configurations also available.

The CATLAB microreactor module range has been designed for the combined roles of catalyst characterisation via a range of dynamic temperature-programmed analyses as well as the rapid, reproducible screening of catalyst activity. The CATLAB microreactor module is provided with seamless on-line, real-time mass spectrometric analysis with data acquisition and analysis via PC under the integrated MASsoft / CATLAB Windows software suite. The microreactor is based around a high temperature Quartz reactor column and integrated air-cooled radiant furnace with close-coupled sampling port for high response and sensitivity. The CATLAB Windows software suite also provides for full microreactor control of temperature (ramp/set-point) and flow with the CATLAB flow control module.

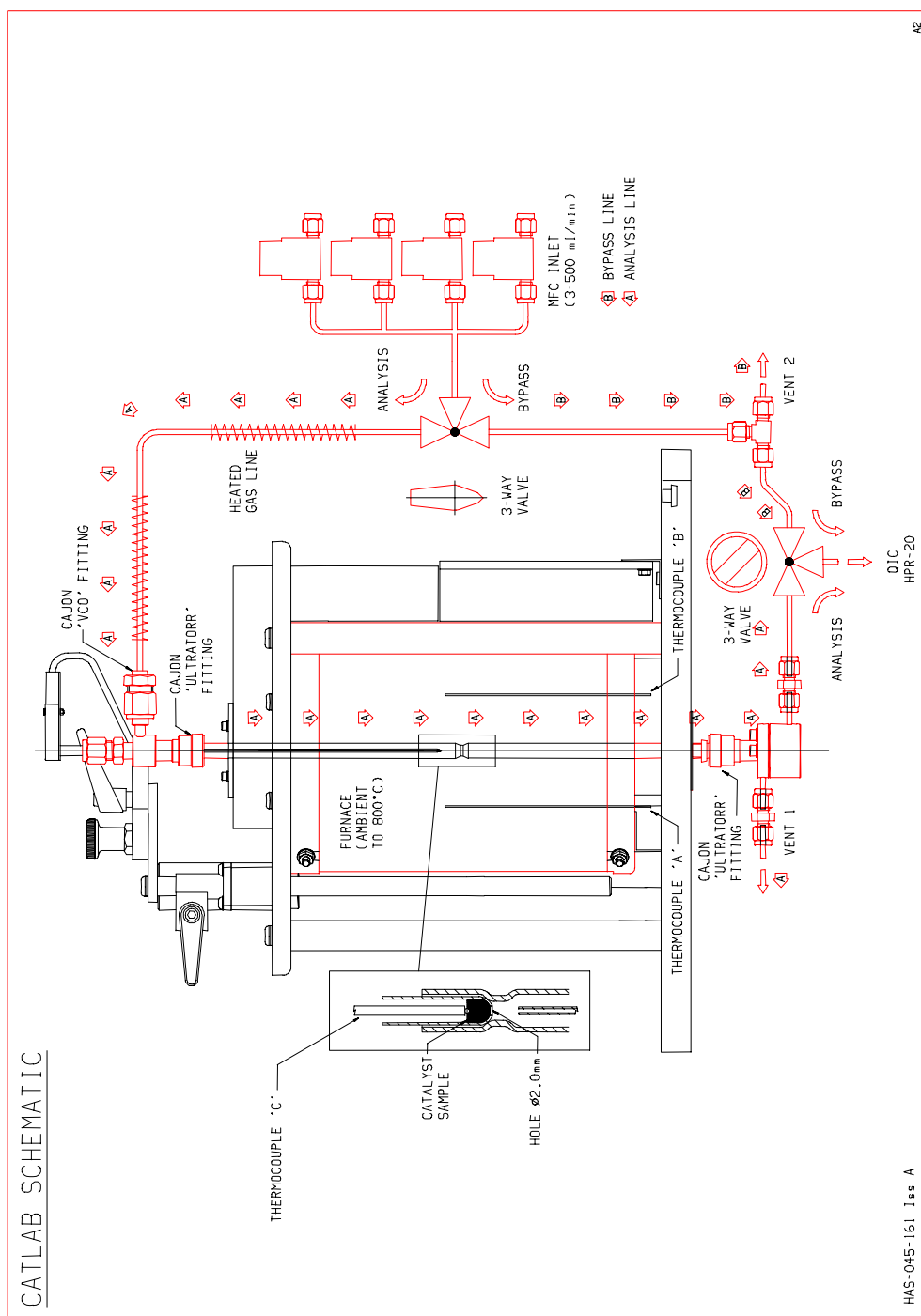
Microreactor

The Hiden CATLAB microreactor is constructed from a high temperature Quartz reactor column incorporating Hiden's Catalyst Cartridge System allowing reproducible sample placement with minimal changeover time.

The microreactor module is based around a fast response, low thermal mass furnace with a temperature range of ambient to 1000 °C at a user defined linear ramp rate of between 1 and 20 °C/min.

- Close coupled hot zone evolved species probe.
- Unique interchangeable catalyst cartridge system.
- 'In-Bed' thermocouple for accurate temperature measurement.
- Shut-off / bypass flow configuration to seal reactor and sampling port.
- Air thermostat and trace heating to minimise condensation on inlet and gas sampling connections for use with vapour species.
- Mass spectrometer response time < 500 ms.

Hidden CATLAB Schematic



Catalyst Characterisation

The Hiden CATLAB is a customisable microreactor system, designed for catalyst characterisation, kinetic and thermodynamic measurements as well as the rapid, reproducible screening of catalyst activity. The system is specifically designed for both isothermal and temperature programmed studies of catalytic systems.

Using a technique known as Gas Adsorption Chromatography the CATLAB is able to directly determine metal surface areas for metals such as copper, nickel (N_2O Reactive Frontal Chromatography), platinum and palladium (CO chemisorption/TPD).

CATLAB also allows the determination of surface coverages as a function of temperature (*e.g.* CO adsorption on $\text{Pt}/\text{Al}_2\text{O}_3$) and also calculate the resulting adsorption isotherms.

Using Temperature Programmed techniques CATLAB can also be used to study energetics, kinetics and reaction mechanisms of catalytic systems.

Technique	Information
Adsorption Isotherms	Coverages, Metal Surface Areas
Temperature Programmed Reduction (TPR)	Reduction Kinetics, Examination of reducible species
Temperature Programmed Desorption (TPD)	Desorption Kinetics, Determination of range/strength/number of active sites
Temperature Programmed Reaction (TPRx)	Reaction Energetics, Optimum reaction temperature, deactivation studies
Temperature Programmed Oxidation (TPO)	Extent of Catalyst Oxidation/Reduction
Temperature Programmed Reaction Spectroscopy (TPRS)	Reaction Mechanisms

Catalyst Screening

CATLAB is also configured for isothermal catalytic reaction studies. The customisable gas manifold can deliver individual or mixtures of reactant gases permitting a range of experimental conditions to be investigated under reproducible conditions. The direct coupling of the CATLAB microreactor to a Hiden mass spectrometer allows the analysis of several different species simultaneously.

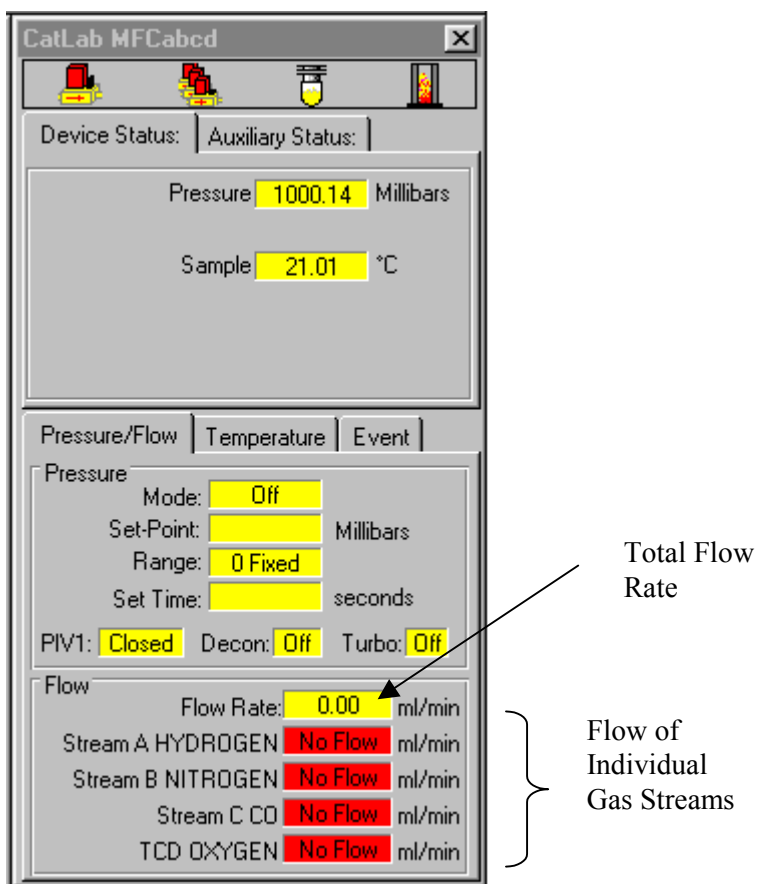
Catalysts can also be characterised post-reaction *in situ* in order to determine changes in the physical properties of the catalyst (*e.g.* metal surface area) caused by the interaction of the reactants with the catalyst. The combination of catalyst characterisation and reaction studies allows the catalyst to be investigated under the same conditions in one piece of equipment without exposure of the sample to atmospheric contamination.

CATLAB Flow Control Module

The Hidden CATLAB microreactor flow control module is customisable to user requirements and comprises of a standard gas manifold with 2, 4, 6 or 8 gas streams. A gas/vapour manifold and corrosion resistant manifold configuration is also available.

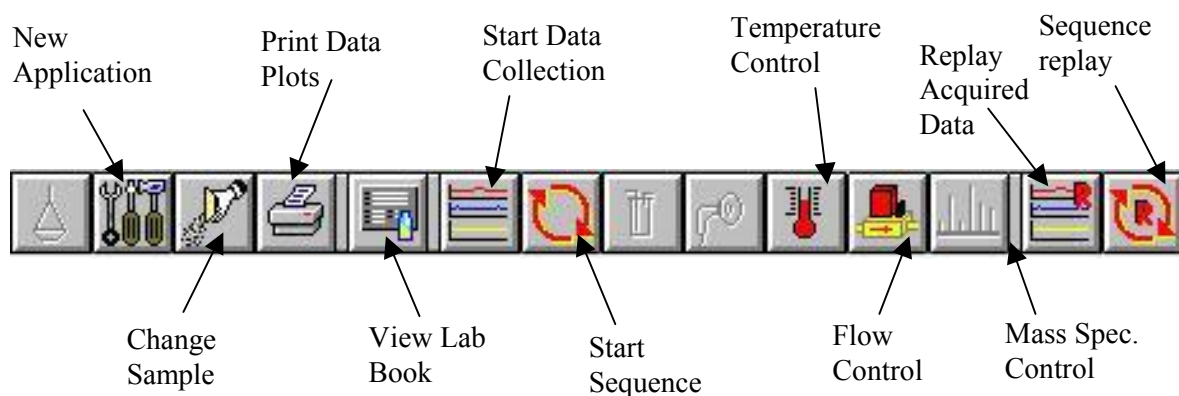
- Flow range: 3-500 ml/min (independently user-specified for each stream).
- Automated control allowing unsupervised operation.
- Corrosion resistant seals available.

Flow Control Display

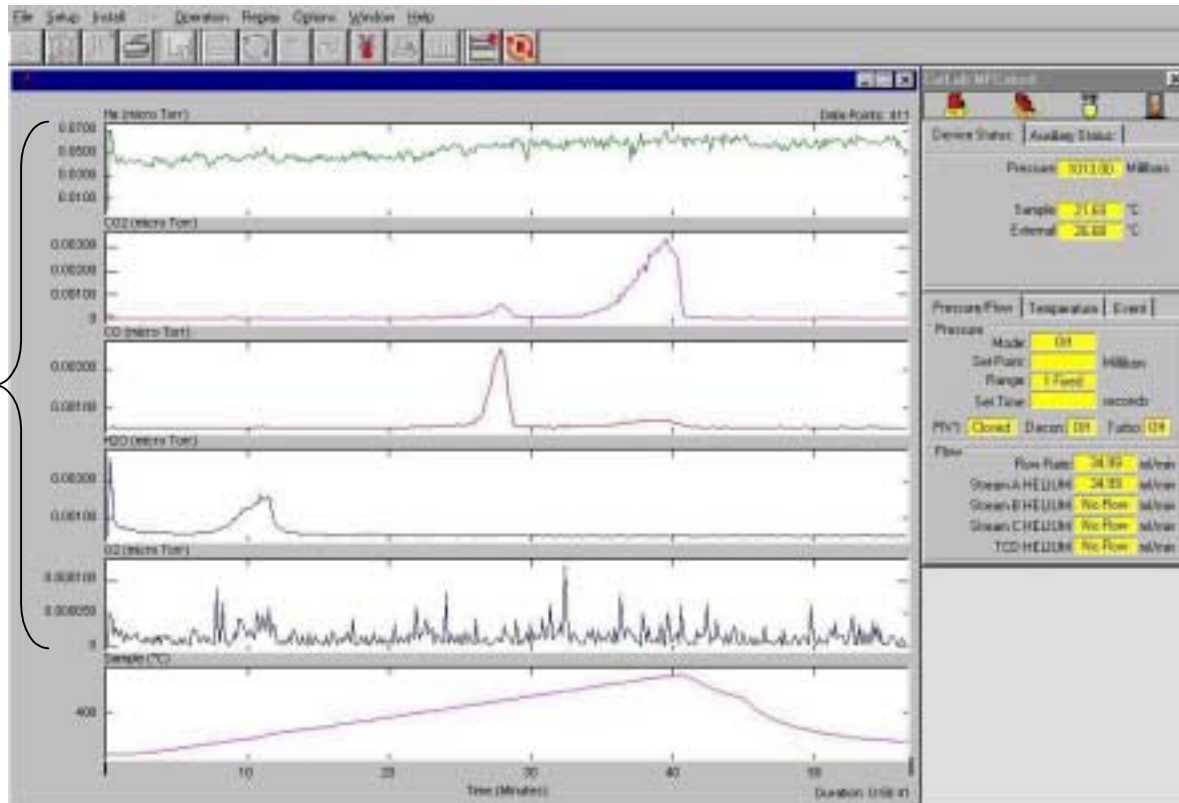


CATLAB Software

The CATLAB microreactor module is provided with seamless on-line, real-time mass spectrometric analysis and data acquisition and analysis via PC under the integrated CATLAB Windows™ software suite. The CATLAB software provides for the full control of the microreactor temperature (ramp/set-point) and gas flow with the CATLAB flow control module.



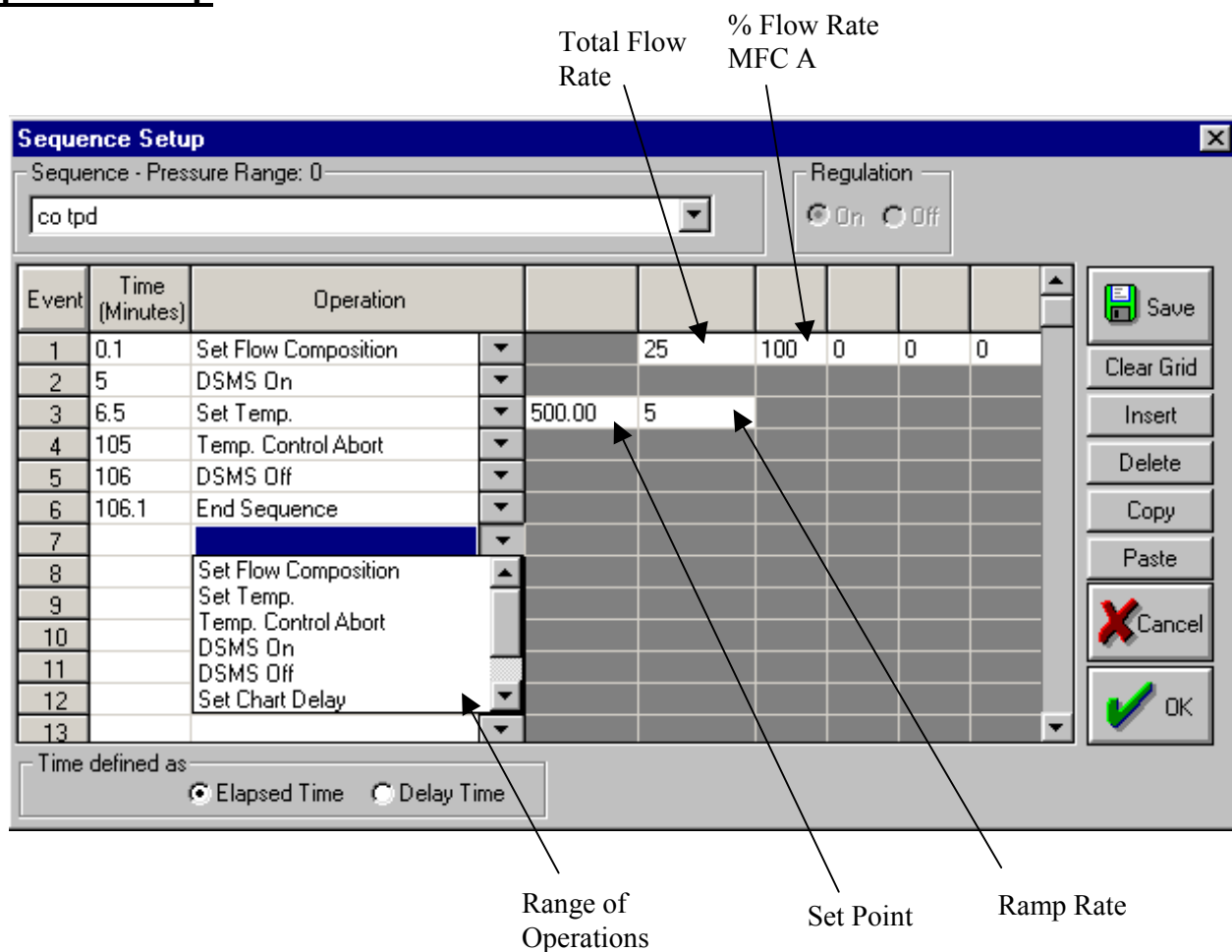
Detected species
Displayed on
Individual
Axes



Automated Control

The Hidden CATLAB offers fully automated control of experimental procedure using user definable sequences, allowing a range of experiments to be performed in one sequence. *e.g.* Pt/Si/O₂ Catalyst activation, CO chemisorption and CO TPD. The sequences allow the continuous unsupervised operation of CATLAB during experiments.

Sequence Set-up



The screenshot shows the 'Sequence Setup' dialog box. The 'Sequence' dropdown is set to 'co tpd'. The 'Regulation' section has 'On' selected. The main table lists events with their times and operations. Annotations point to specific values: 'Total Flow Rate' points to 25, '% Flow Rate MFC A' points to 100, 'Set Point' points to 5, and 'Ramp Rate' points to 5. The 'Range of Operations' points to the 'Set Chart Delay' operation in the table. The 'Time defined as' section has 'Elapsed Time' selected.

Event	Time (Minutes)	Operation	Total Flow Rate	% Flow Rate MFC A	Set Point	Ramp Rate
1	0.1	Set Flow Composition	25	100	0	0
2	5	DSMS On				
3	6.5	Set Temp.	500.00	5		
4	105	Temp. Control Abort				
5	106	DSMS Off				
6	106.1	End Sequence				
7						
8		Set Flow Composition				
9		Set Temp.				
10		Temp. Control Abort				
11		DSMS On				
12		DSMS Off				
13		Set Chart Delay				

Annotations:

- Total Flow Rate: 25
- % Flow Rate MFC A: 100
- Set Point: 5
- Ramp Rate: 5
- Range of Operations: Set Chart Delay

Buttons: Save, Clear Grid, Insert, Delete, Copy, Paste, Cancel, OK.

Time defined as: ☒ Elapsed Time ☐ Delay Time

Catalyst Characterisation and Screening Primer

CATLAB provides for the combined characterisation and screening of catalysts. The characterisation methods involved are based on Temperature Programmed Studies – A series of thermal characterisation methodologies including *Temperature Programmed Desorption* (TPD), *TP-Reduction* (TPR), *TP-Oxidation* (TPO) and *TP-Reaction* (TPRx). In addition CATLAB allows analyses of adsorption phenomena (including determination the isosteric enthalpy of adsorption), determination of active metal area by N₂O titration / frontal chromatography as well as conventional kinetic and activity screening studies.

TPD

TPD analysis identifies the strength, number and the type of active sites on a *catalyst*. It entails the analysis of the desorption of adsorbates as the sample is heated. Desorption occurs at characteristic temperatures when the adsorbate contains sufficient energy to overcome the *activation energy of desorption* and dissociate the bond between the active site and adsorbate to provide direct information regarding the strength of the interaction between the *active sites* and probe gas i.e. the *enthalpy of adsorption* as well as the *coverage* θ . In addition knowledge of the stoichiometry of the gas /solid reaction enables quantification of the total number of active sites that are available on the catalyst surface.

Redhead Model of TPD – The Redhead model (P.A. Redhead, *Vacuum* **12**, 203, 1963) is based on the assumption that the desorption process follows a simple power rate equation:

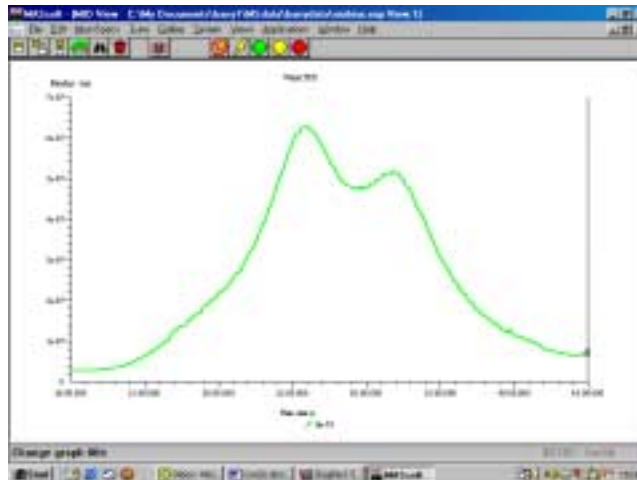
$$\frac{r_d}{N_s} = -\frac{d\theta_A}{dt} = k_0 \exp\left(\frac{-E_A}{kT}\right)\theta_A^n$$

The right hand side of the equation is the product of an Arrhenius rate constant, the pre-exponential k_0 and the temperature dependent exponential factor, with a power of the coverage. The symbols are defined as follows.

- r_d is the rate of desorption of species A
- N_s is the concentration of surface adsorption sites.
- θ_A is the coverage of species A on adsorption sites
- t is the time (the independent variable of the rate process).
- k_0 is a pre-exponential factor (depends on atomic masses and bond strengths in A).
- T is the temperature in Kelvin (K).
- n is the order of the desorption reaction (power of the rate law). First order: $n=1$, etc.
- E_A is the activation energy per mole for desorption of A. Alternatively, ϵ_A - per molecule
- k or k_B is the Boltzmann constant (per molecule), $1.38066 \times 10^{-23} \text{ J K}^{-1}$.
- Alternatively, $R (=N_A k_B)$ per mole, $1.31451 \text{ J K}^{-1} \text{ mol}^{-1}$
- N_A is Avogadro's number, 6.02214×10^{23} .

To use the Redhead model, one solves the rate expression for $\theta_A(t)$, coverage versus time.

Example TPD - Water desorption



The 2 distinct peaks correspond to discrete sites of different adsorption strengths. CATLAB software allows integration (linear or assumed / forced horizontal baseline) of each peak under direct mouse selection to determine coverage (θ).

This entails equating the area to a rectangle of dimensions $H_c \times t$ (H_c = calibration height and is measured, t = time in s), thus:

$$\frac{\text{area}}{H_c} = \text{time} \quad \text{and} \quad \text{time} \times \text{flowrate} = \text{volume}$$

rearranging $pV = nRT$ to $n = \frac{pV}{RT}$

From this we can determine the number of atoms / molecules $Y = n \times N_A$ (Avogadro)

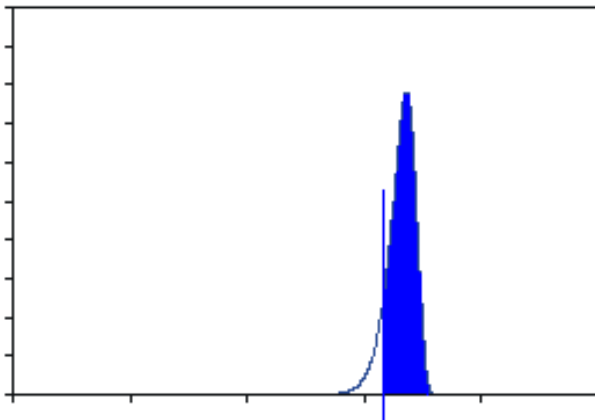
This allows determine of coverage θ in 2 forms:

$$\frac{Y}{M_n} \times 100$$

Where M_n = number of molecules corresponding to full metal coverage (from the metal area calculation).
Or in terms of area per gram

$$\theta_{\text{area}} = \frac{Y}{\text{mass} \times \text{BET area per gram}}$$

Once coverage has been determined it is possible to determine the heat of desorption. To do this we sample a series of temperature increments and integrate the concentration of remaining adsorbate i.e. the shaded area below.



Then using the equation
$$h = k\theta^z$$

Where h = height of the MS response at temperature T and θ the shaded area and z the order of desorption (see below for determination of order of desorption).

Hence from the Arrhenius equation
$$k = Ae^{\frac{-E}{RT}}$$

Where E = the Heat of Desorption

Therefore
$$h = Ae^{\frac{-E}{RT}} \text{Area}^z$$

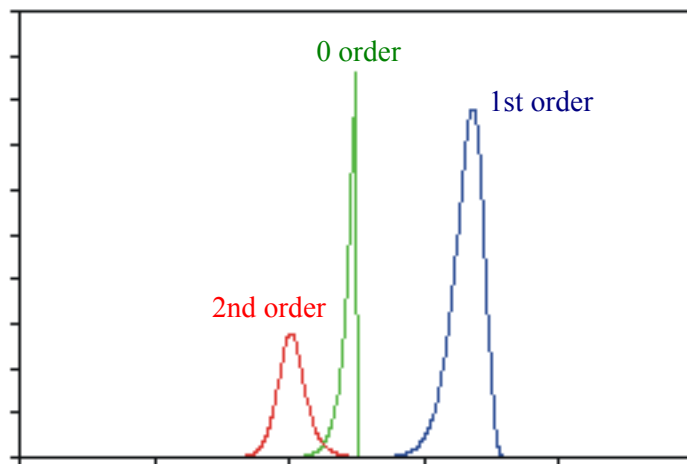
Or
$$\ln h = \ln A - \frac{E}{RT} + \ln \text{Area}^z$$

i.e.
$$\ln \left[\frac{h}{\text{area}^z} \right] = \ln A - \frac{E}{RT}$$

Therefore a plot of $\ln \left[\frac{h}{\text{area}^z} \right]$ vs. $\frac{1}{T}$ gives a straight line of gradient $-\frac{E}{R}$ and intercept $\ln A + \ln \left[\frac{k_2}{k_1} \right]$.

Nb. $\ln(k_1/k_2)$ is added to account for the calibration constants height of area (respectively) to rationalise the values used in the calculation of area from θ .

In addition CATLAB can analyse peak shape to determine the order of desorption e.g.



Zero Order Peaks – Display a leading edge and a sharp cut-off after the peak maxima.

First Order Peaks – Again display a leading edge with more gradual decrease, integration of the 2 peak halves shows a non-symmetrical aspect with an approximate 60:40 split. (Note in this case an estimate of desorption energy is obtained in KJmol^{-1} from $E_d = T_{\text{max}} \times 0.28$)

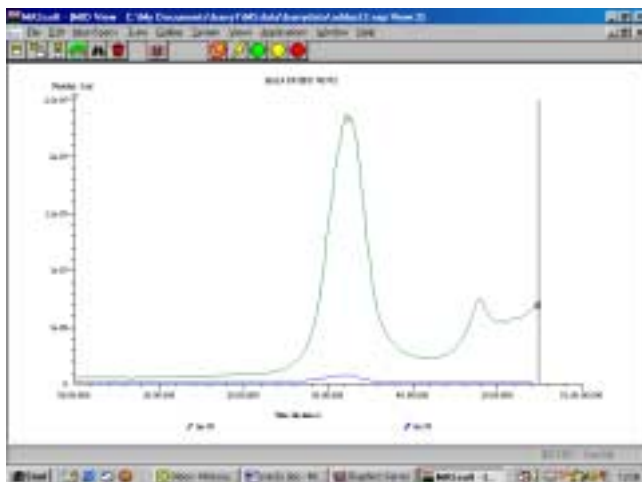
Second Order Peaks - Peak is symmetrical about the desorption maximum.

TPR / TPO

TPR/TPO methods are complimentary and examine the reduction – oxidation (redox) characteristics of a catalyst. In addition they allow analysis of any interactions between the supported precursor phases and the *support*. TPR/TPO is particularly useful for the study of interactions between the components in multi-metallic systems and for the evaluation of the role of *promoters* (alloy formations or promotion effects).

TPR entails exposing an oxidized catalyst or catalyst precursor to a (linear) programmed temperature rise, under a flow of dilute reductant gas mixture (typically H_2 / Ar). TPO is somewhat similar except the sample is in the reduced form and exposed to a dilute oxidant (e.g. O_2/He), again under a programmed temperature increase. The reduction / oxidation rates are monitored by analysis of the change in composition of the reactor effluent with any change in H_2 or O_2 concentration directly monitoring reaction progress. The use of low partial pressures of the reactant makes it possible to observe the intermediate reactions, depending on TP conditions e.g. ramp rate and flow rates and concentration of reactive gas while the temperatures at which the reduction / oxidation occur are indicative of the strength of surface bonds, as shown for the TPO of NH_3 where 2 distinct species are present. TPR/TPO provide for both qualitative and quantitative analysis and the ‘spectra’ produced are characteristic for a given solid. TPR is more widely used than TPO, but for quantitative studies the use of these analyses in succession i.e. hydrogen/oxygen titration is appropriate and allows calculation of the metal phase percentage in the catalyst (if the stoichiometry of the reaction is known). A further benefit of combining the two methods is that

TPO acts as a *calcination* to remove undesired contaminants which may affect on the reactivity of the catalyst active phase.

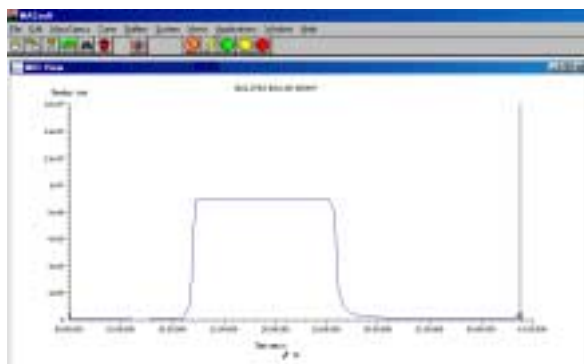


TPReaction

TPRx is closely related to TPD but entails co-adsorption of species to monitor their interactions and reactions on the surface.

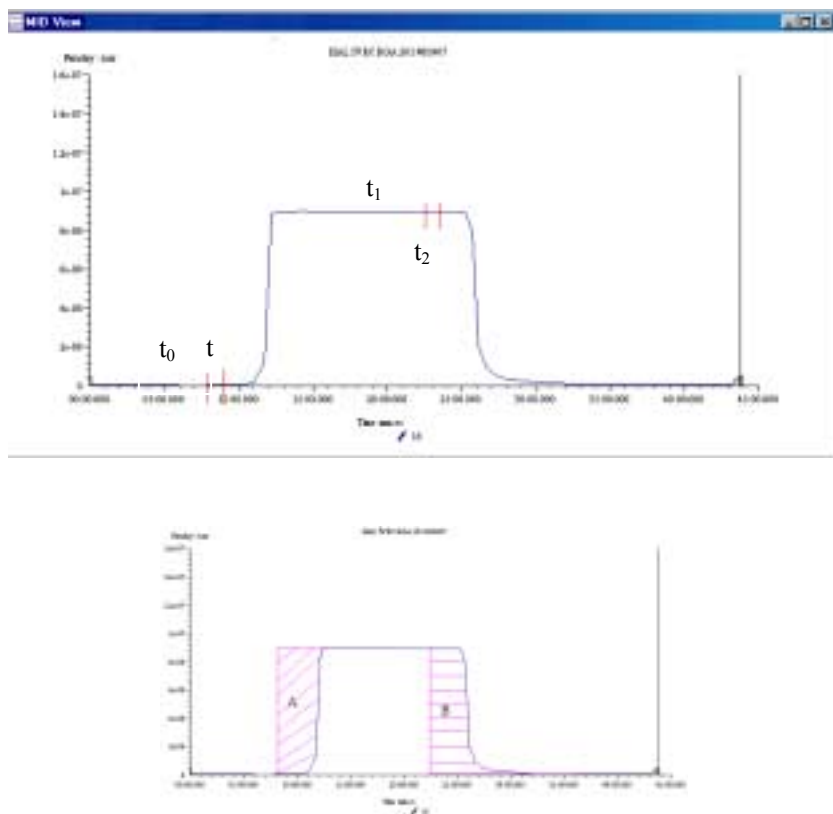
Adsorption Plots

If a gas is adsorbed onto a sample for a period of time and this adsorption is recorded along with the trailing edges then the plot will look like this:



The plot shows the adsorption of ammonia (following mass 16) onto a vanadium pyrophosphate catalyst at 60°C. Such a plot is obtained by first passing helium through the system, then switching to ammonia at some known time t_0 . The time to sweep out the dead volume is given by $t - t_0$. The plot shows that the ammonia is adsorbed by the surface for some period of time and then the adsorption ceases and the ammonia signal breaks through to give the square wave shown. At some later point t_1 the flow of reactant gases is switched from ammonia back to

helium and the trailing edge of the adsorbate (in this case ammonia) is observed and recorded. Again the time to sweep out the dead volume must be accounted for thus the trailing edge actually begins at the point t_2 . The trailing edge will continue to be observed until the adsorbant gas returns to its baseline i.e the value exhibited before t_0 .



This plot is isothermal (constant temperature) and can yield various pieces of information.

First we need to find areas A and B and ensure that they are equal. If however area A is greater than area B then we need to add (A-B) to area B.

By performing a stripwise integration of area B we can obtain an adsorption isotherm. Then if we rearrange $pV = nRT$ into

$$\frac{n}{V} = \frac{P}{RT} = \text{concentration}$$

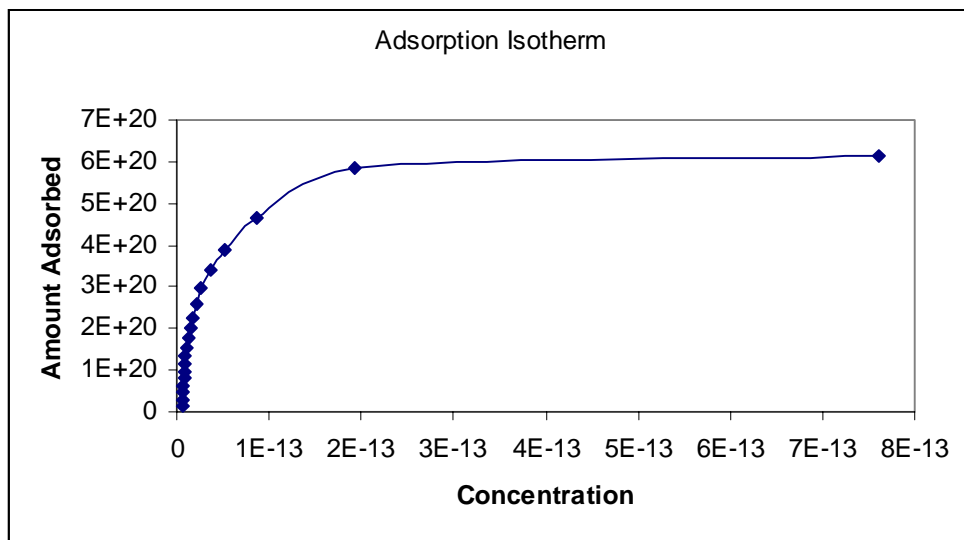
and use this to find the amount adsorbed from the area of the strip using:

$$\frac{\text{area}}{h_c} = \text{time} \quad \text{and} \quad \text{time} \times \text{flowrate} = \text{volume}$$

$$\frac{pV}{RT} = n$$

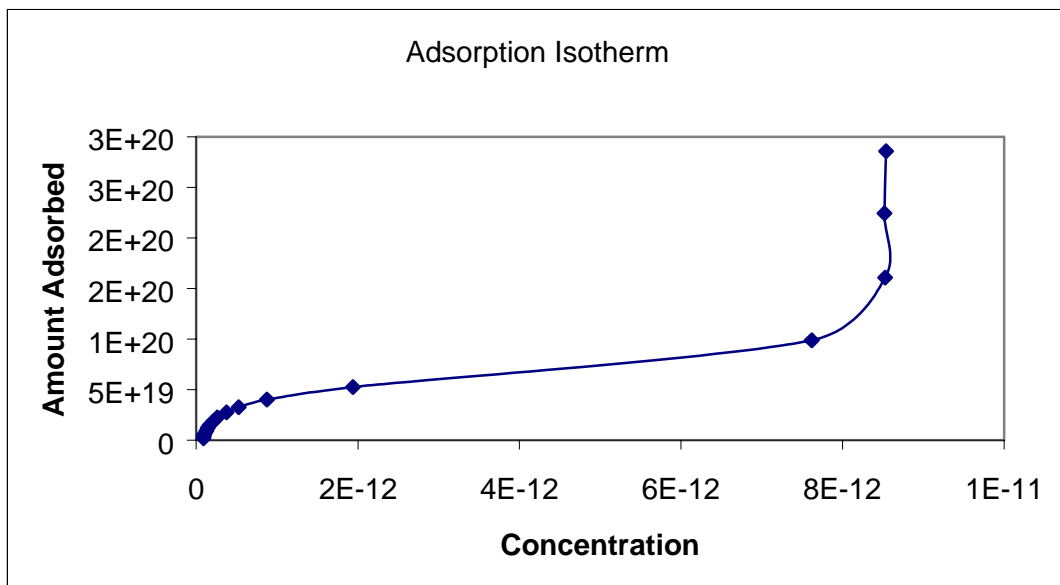
Where n = number of moles adsorbed. Then a plot n vs. p/RT gives:

This gives us the isotherm at that temperature.

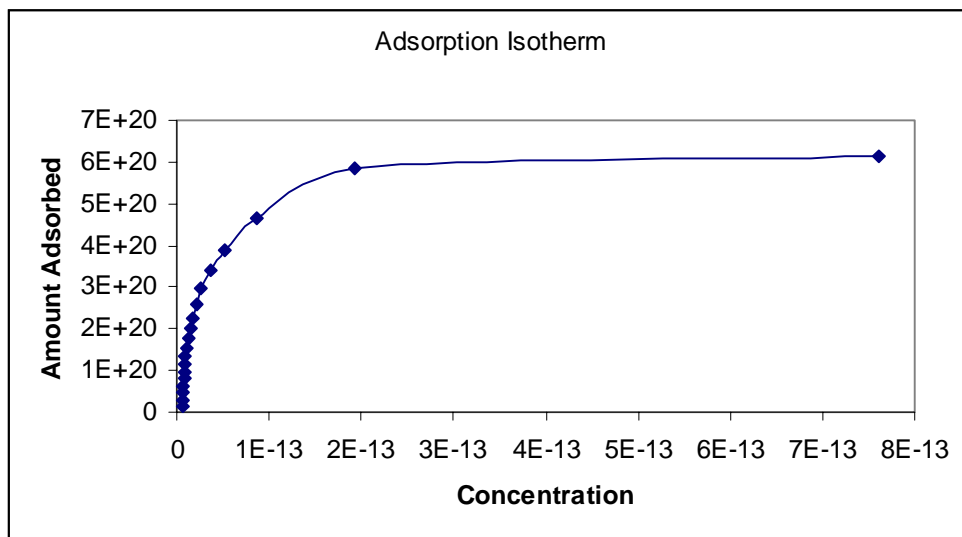


N.B

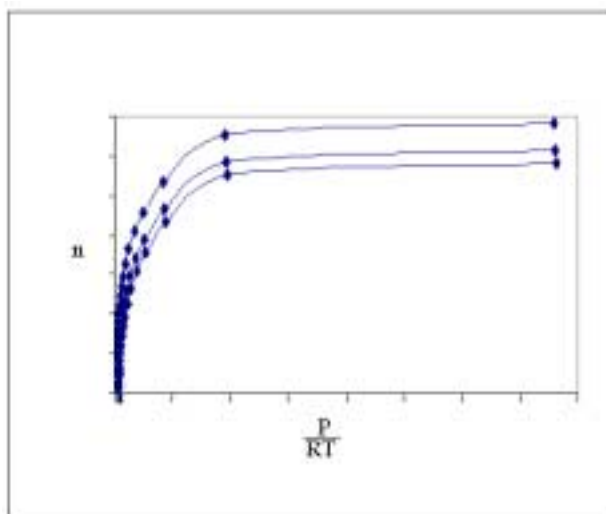
It is often the case that, due to the high accuracy of the calculation, within the software that the last few points of the isotherm appear to be a vertical line. This is due to fact that the final variables will inevitably yield identical or very close to identical x-axis values as they are all baseline values with similar pressure values (the y-axis values of the original plot obtained from the HAL 4) i.e an asymptotic limit has been reached e.g:



If such points do occur they can be easily deleted in Excel to give the clearer form of the isotherm i.e.:



If this experiment is repeated at various temperatures and all the various temperatures and all the isotherms are obtained then we can plot them all together to give:



A plot of this kind is useful in determining the heat of adsorption using the following method:

If we then pick a known coverage, θ , and plot $\ln \frac{1}{p}$ vs. $\frac{1}{T}$ it will enable us to solve:

$$\ln A + \frac{\Delta H}{RT} = \ln \left(\frac{\theta}{1 - \theta} \right) + \ln \left(\frac{1}{p} \right)$$

Thus the plot is of the line of equation:

$$\ln\left(\frac{1}{p}\right) = \frac{\Delta H}{RT} + \left[\ln A - \ln\left(\frac{\theta}{1-\theta}\right) \right]$$

Therefore the gradient of this plot will give the adsorption enthalpy (ΔH) and the intercept, I, will give A the pre-exponential by rearranging:

$$I = \ln A - \ln \frac{\theta}{1-\theta}$$

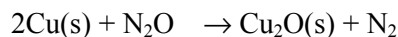
to give:

$$\exp\left[I - \ln\left(\frac{\theta}{1-\theta}\right) \right] = A$$

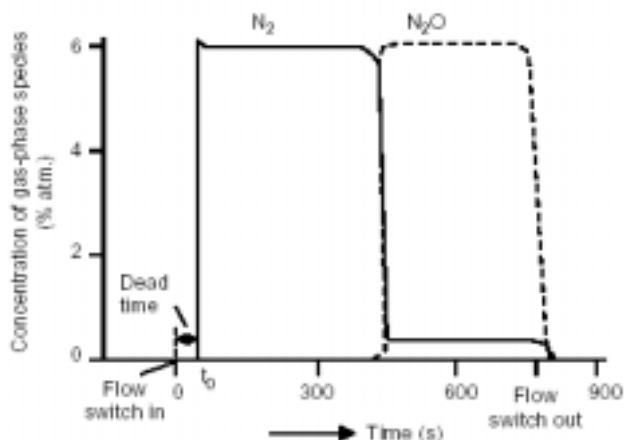
Metal Surface Area from N₂O Frontal Chromatography

CATLAB provides for quantification of metal surface area by the titration of pre-reduced metal using N₂O chemisorption.

For example for Cu



An idealised example of this process is shown below:



If we find the N₂ evolution area and then perform and assume 100% conversion we can determine the Metal Surface area:

$$\frac{\text{area}}{h_c} = \text{time} \quad \text{and} \quad \text{time} \times \text{flowrate} = \text{volume}$$

Then rearrange $pV = nRT$ to $n = \frac{pV}{RT}$

We find the number of moles (n) and hence the number of molecules by multiplying by Avagadro's number (N_A).

$$Y = n \times N_A$$

Where Y = number of molecules.

Given that Cu/Ni has 5×10^{18} oxygen atoms. Therefore:

$$\text{Metal Surface Area} / \text{m}^2 = \frac{Y}{5 \times 10^{18}}$$

Note using this method we can also express metal content as a dispersion where:

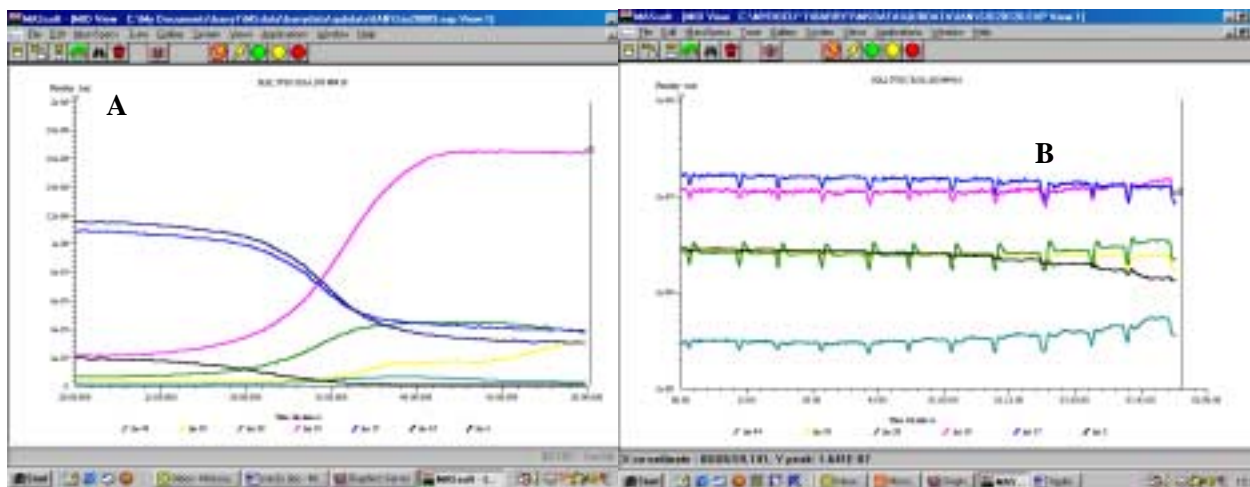
$$\% \text{ dispersion} = 100 \times \frac{\text{number of exposed surface atoms}}{\text{total number of atoms of material}}$$

Catalyst Screening & Kinetic Studies

The characterisation of catalytic materials can provide fundamental understanding of the mechanism of operation and/or desirable qualities for a catalyst. However, in most cases, the main characteristic of a catalyst is that it is efficient as possible for its intended purpose. This may entail that it exhibits high activity / conversion / turnover (number of reactions / s on a site) or a high selectivity wrt a specific product or process, or indeed all of these attributes. The process of identification of such materials is known as screening.

Screening may be performed either isothermally or as a function of reaction temperature, in continuously flowing reagent (c.f. TPReaction where the reagents are adsorbed only once) and the performance / evolution of products monitored. However that for any true comparison to be made the catalysts under study should be examined at the same rate of deactivation and any selectivities compared at similar conversion levels. An example of a temperature profile of a catalyst for NH_3 oxidation is shown in Figure A: This shows increasing oxidation of the NH_3 with temperature as well as the temperature response of the possible products N_2 , NO , N_2O and NO_2 , with increasing levels of undesirable oxides of nitrogen being produced at higher temperatures.

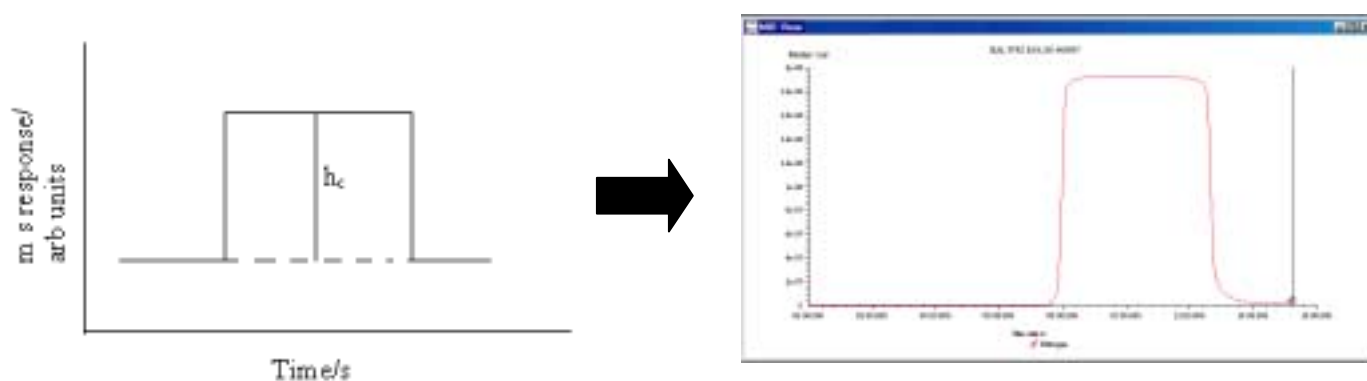
CATLAB also provides for standard kinetic studies to enable determination of the orders of reaction of reagents to be determined, and rate-determining step(s) investigated by examination of the temperature response of reactivity as a function of component concentration (with all other conditions constant so as not to affect rate). Again however there is a caveat since for any true kinetic analysis, all studies should be performed under differential conditions i.e. conversion < 20% to avoid heat and mass transfer. An example is shown below for NH_3 oxidation (Fig B). Herein we see a series of steps of reaction, each step corresponding to a 5 °C increase in temperature for the reaction of 1000 ppm NH_3 in 5% oxygen, with this set of reactions forming part of a 'map' of reactions in which the concentration of NH_3 was varied, at constant O_2 and the rate and selectivity examined. These experiments confirmed that activation of the NH_3 was rate limiting and that increasing temperature or decreasing NH_3/O_2 favoured NO production.



Appendix - Calibrations

All calculations require some sort of calibration value in order to produce meaningful results from spectra that are plotted in arbitrary units. Therefore in order to do these calculations the user must have values for a “blank” catalyst – one that does not react i.e. adsorb or desorb the species. This is either accomplished by performing the experiments on an empty reactor tube or on a reactor tube filled with glass beads.

By passing the reactant gases through this blank you can obtain a plot for each of the gases:



Where h_c = calibration height.

To find the time to sweep out the dead volume again you can use a blank and switch from one gas to another and time how long from switching time to the time you obtain a signal response on the mass spectrometer.

Calibration areas are obtained in the same manner:



Glossary

Activation Energy – the activation energy is the energy that a system must acquire in order for a reaction to proceed via its transition state. It is a mathematically defined quantity that shows the dependence of a rate constant on the temperature according to:

$$E_a = RT^2 \left(\frac{\partial \ln k}{\partial T} \right)_\theta$$

Which in turn is derived from the Arrhenius equation:

$$k = A \exp \left(\frac{-E_a}{RT} \right)$$

Where A is the pre-exponential factor.

Active Sites - A catalyst surface is made up of locations (sites) on the surface. The sites where the reaction takes place are known as active sites. In the case where different (sometimes competing) reactions take place some reactions will take place at specific sites and not others.

Acid Sites – can be defined as an electron acceptor (Lewis acid *e.g.* coordinatively unsaturated Al^{3+} ions of an alumina surface) or proton donor (Brønsted acid *e.g.* surface hydroxyl groups of chromia)

Activity – The rate at which the reactants are consumed.

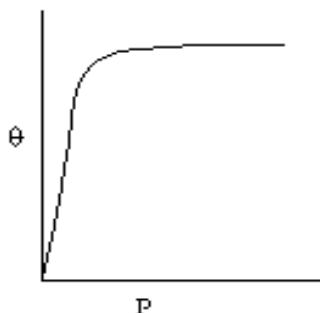
Adsorbate – This refers to the substance that is adsorbed onto the surface of the substrate.

Adsorbent – A surface onto which a reactant can be adsorbed.

Adsorption - This refers to the condensation/accumulation of gases, liquids or solutes on the surface of a solid. It can be classed as **physisorption** (the formation of a weak bond held by van der Waals forces *e.g.* bonding of an inert gas (N_2) at low temperatures) or **chemisorption** (the formation of a chemical bond to the surface by an adsorbate).

Adsorption Isotherm – The relationship between the amount of material adsorbed and that present in the gas phase. There are various types of these plots including:

- **Langmuir Isotherm** – When a gas is adsorbed at a temperature well above the boiling point of the gas onto a non-porous solid a Langmuir adsorption isotherm is usually produced



Where θ = Fractional Surface Coverage and P = Pressure.

However not all adsorption isotherms take this form. Here we assume that there is an energetic equivalence between the adsorption sites and this is rarely the case. Particularly due to the fact that surfaces are not usually atomically smooth therefore the adsorbing molecule will react first (and most energetically) with atoms/ions of low coordination number with molecules arriving later being unable to interact so strongly. In order to negate this assumption other isotherms have been designed including:

- **Tempkin Isotherm**

$$\theta = k_1 \ln(k_2 bP)$$

k_1 and k_2 are constants whose values depend on initial enthalpy adsorption.

This isotherm supposes a linear decrease of enthalpy of adsorption with coverage.

- **Freundlich Isotherm**

$$\theta = kP^{\frac{1}{n}}$$

This assumes a logarithmic decrease (k and n are constants with $n > 1$). However this is also flawed in that it does not predict a limiting value for θ and is therefore unrealistic. However it is often accurate between values of 0.2 and 0.8.

- **BET Isotherm** - This looks at multilayer adsorption assuming monolayer treatment can be extended to multilayer adsorption. this is done by assuming each adsorbed species in the first layer is a site for adsorption into the second layer and each species in the second layer serves the third layer and so on and so forth. Then by equating the rate of condensation (adsorption) on the bare surface to the rate of evaporation (desorption) a mathematical expression may be formed for each layer. These formulae can then be put together to give the “simple” form of the BET equation:

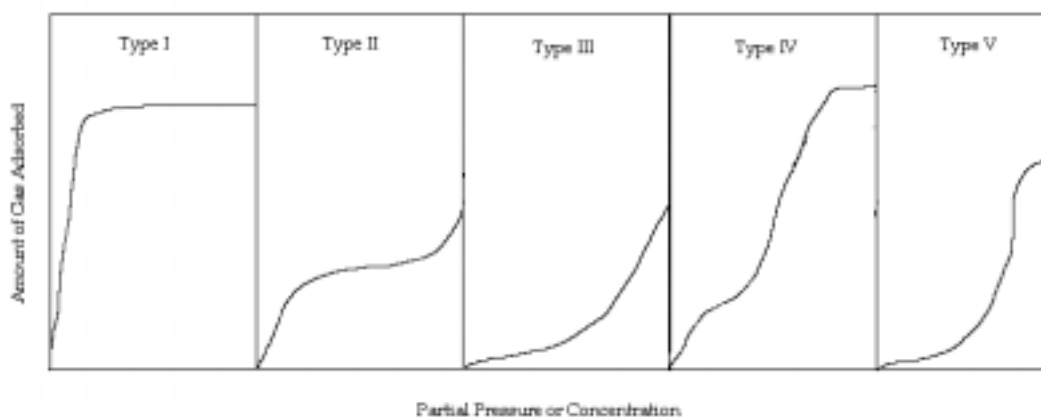
$$\frac{p}{x(p_0 - p)} = \frac{1}{x_m C} + \frac{C-1}{x_m C} \frac{p}{p_0}$$

Where x_m = monolayer capacity

p_0 = saturated vapour pressure of the adsorbing gas at the temperature used

C = constant

According to the BET method isotherms can be classified into 5 distinct groups:



Hysteresis Loops – These isotherms occur from type IV BET isotherms as a result of the isotherm not following the same route in desorption as it does in adsorption. This is due to the fact evaporation of a condensed gas in fine pores does not occur as easily as it condenses – a molecule evaporating from a highly curved meniscus has a higher probability of re-condensing than one evaporating from a plane surface.

Calcination – This occurs when a solid is heating to just below its melting point in order to change its composition or remove the inactive component of the catalyst precursor.

Catalyst – A substance that increases the rate at which a reaction reaches equilibrium without being consumed in the process. Catalysts can be **Homogeneous** (the same phase as the reactants e.g. fluid reactants and fluid catalyst) or **Heterogeneous** (a different phase to the reactants e.g. gaseous reactants and solid catalyst).

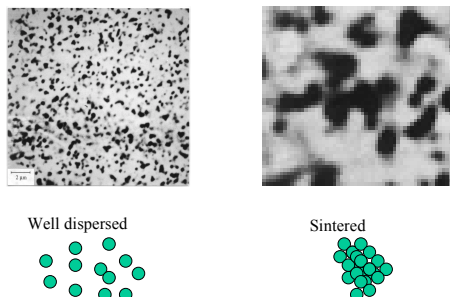
Conversion – This refers to the fraction of reactants converted into products.

Deactivation – This refers to the undesirable loss in activity of the catalytic species. It can be achieved by various methods including:

Poisoning/ Fouling- this occurs when an impurity is adsorbed onto the catalyst surface thus blocking an active site and rendering it useless. A poison is much more strongly adsorbed than a reactant and therefore denies the reactant access to the surface site.

Sintering – To form a coherent mass by heating without melting. Sintering occurs when smaller crystallites being unstable at elevated temperatures so that they migrate and coalesce, thus becoming larger. (This does not necessarily occur at particularly high temperatures).

Catalyst before and after sintering

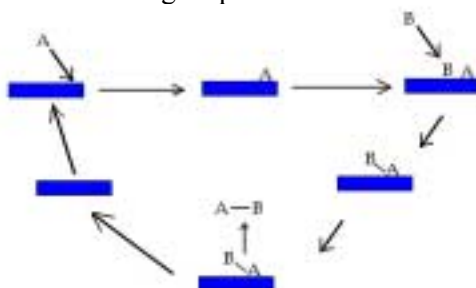


Desorption – This is the process of the removal of an adsorbate from the surface either by thermal or other forms of inducement.

Enthalpy Of Adsorption – A thermodynamic property, which gives the amount of heat lost or gained during adsorption of a gas onto a surface.

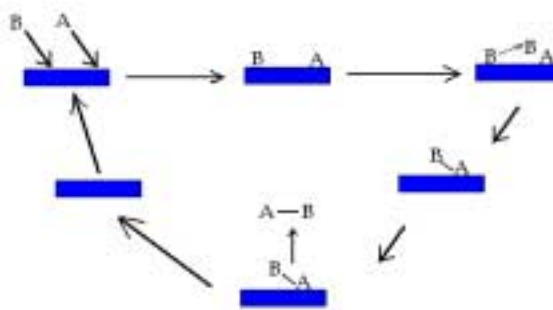
Mechanism – This refers to the course reagents take in order to transform into products. In catalysis there are three main mechanisms:

- Eley – Rideal Mechanism – This mechanism of catalytic action suggests that gas phase species collide with adsorbed species and react to give products.

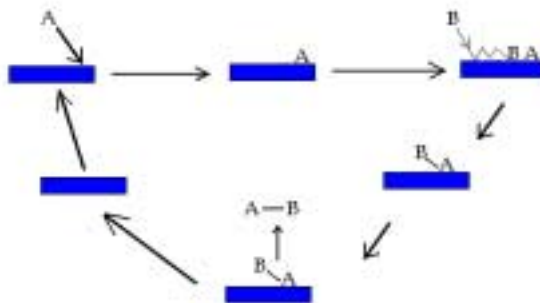


i.e. reactant A chemisorbs onto the catalyst surface then reacts with molecule B to form an A-B complex which then in turn desorbs to give A-B and the cycle continues, *e.g.* $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2$. This reaction can also occur in reverse *i.e.* adsorbing A-B to give A and B.

- Langmuir-Hinshelwood Mechanism – In this mechanism of catalytic action both reagents A and B adsorb onto the catalyst surface. They then react to form a complex A-B, which is then desorbed to give A-B.



- Precursor Mechanism – In this mode of catalyst action A adsorbs first than this is followed by B colliding with the surface to enter a mobile precursor state. This precursor rebounds along the surface until it encounters an adsorbed A molecule. This precursor then reacts with A to form an A-B complex which in turn desorbs to give A-B e.g. $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$.



Metal Surface Area – The area occupied by a metal on the surface of a catalyst. Nickel and copper areas can be quantified by the adsorption of N_2O at 60°C to calculate the number of metal atoms present and thus the area can be calculated. Metals such as platinum and palladium can be measured by the adsorption of CO. i.e a metal surface area is quantified by adsorbing a gas that will adsorb solely onto the metal and then quantifying the number of atoms adsorbed and thus the area occupied.

Overall order of reaction – This is the sum of the orders for all of the reactants. *i.e.* if

$r = k[A]^n[B]^m[C]^p$ then the overall order of the reaction is $n + m + p$.

Oxidation – This refers to the increase in oxidation number, which may in turn correspond to a loss of electrons.

Rate Constant (K) – The constant used in the rate equation and other catalytic calculations *e.g.*

$$r = -k[A]^n \qquad k = A \exp\left[\frac{-E}{RT}\right]$$

Rate Determining Step - This is the slowest step in a multi-step mechanism. It is the step that determines the overall rate of reaction.

Rate Equation – An equation that describes the relationship between concentration of all species present in the reaction and the rate of the reaction i.e. rate as a function of concentration.

$$r = k[A]^n$$

[A] = concentration of A (mol/dm³)
n = order of reaction
k = rate constant.

Rate Law Expression - This refers to the equation relating the rate of the reaction to the concentrations of the reactants and the specific rate of the constant.

Rate of Reaction - This refers to the change in concentration of a reactant or product per unit time.

Reduction – A decrease of the oxidation number, corresponding to a gain of electrons.

Selectivity – The selectivity of a product is the fraction that it constitutes within the total products.

Support – The support is the vehicle for the active phase of any promoters that may be present. It has many functions including maximising the surface area of the active phase by providing a large area over which it may be spread and to allow the active phase and the promoters to be cast in the form of a coarse particle suitable for use in fixed bed reactors. Normally the catalyst support is catalytically inactive on its own but when coupled with the active phase it can participate in the total reaction in important ways.

Turnover Frequency – This is an expression for rate in terms of the molecules reacted per site per second.

$$T = A_{SV} N_A$$

A_{SV} = Specific Activity N_A = Avagadro's number

Although T is used academically one must be cautious in its use as it does not represent effectiveness in catalysis accurately namely because it is possible to have a catalyst with high turnover but low surface area per unit volume *i.e.* T is high but activity is low.

Definitions taken from

- IUPAC Compendium of Chemical Terminology
- Heterogeneous Catalysis Principles and Applications (G C Bond)
- Introduction to the Principles of Heterogeneous Catalysis (Thomas and Thomas)
- The Basis and Application of Heterogeneous Catalysis (M Bowker)
- Chemical kinetics and Catalysis
- www.shellglobalsolutions.com
- <http://biospace.intota.com>