Surface Science
CATLAB Tech Info Sheet 162

CATLAB Techniques

Temperature Programmed Techniques With the Hiden CATLAB

Temperature Programmed Techniques

For catalyst characterisation CATLAB uses methods based on Temperature Programmed Studies – A series of thermal characterisation methodologies including:

- *Temperature Programmed Desorption* (TPD)
- *TP-Reduction* (TPR)
- *TP-Oxidation* (TPO)
- *TP-Reaction* (TPRx)

Additionally, CATLAB allows analyses of adsorption phenomena (including determination the isosteric enthalpy of adsorption), determination of active metal area by N_2O titration / frontal chromatography as well as conventional kinetic and activity screening studies. The techniques and the information obtained by using these techniques are described in this technical note.

Catalyst characterisation techniques using pulse chemisorption methods are also available using the CATLAB – PCS. See Tech Info Sheet 160.

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Technique	Information
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, Reaction Mechanisms Optimum reaction temperature, Deactivation Studies
Temperature Programmed Oxidation (TPO)	Extent of Catalyst Oxidation/Reduction

TPO/TPR

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 (e.g. H_2 / Ar). An example from a NiMgO TPR is shown in Figure 1.

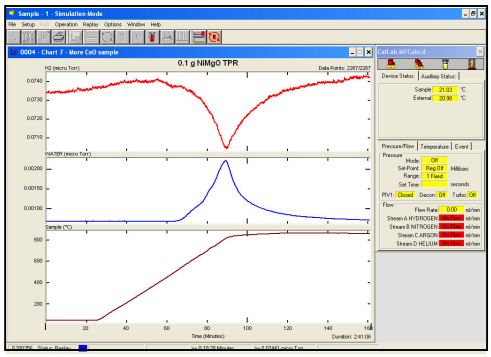

Figure 1 TPR from a NiMgO Catalyst

TPO is 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 conditions *e.g.* ramp rate, flow rates and concentration of reactive gas, while the temperatures at which the reduction / oxidation occur are indicative of the strength of surface bonds. 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 that may affect on the reactivity of the catalyst active phase.

TPD

TPD analysis identifies the strength, number and type of active sites on a catalyst. It entails the analysis of the desorption of adsorbates as the sample is heated under a linear temperature ramp. 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. Additionally, 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.

The advantage of using a mass spectrometer over other detectors such as thermal conductivity detectors (TCDs) is that the mass spectrometer can identify more than one species desorbing from a catalyst surface.

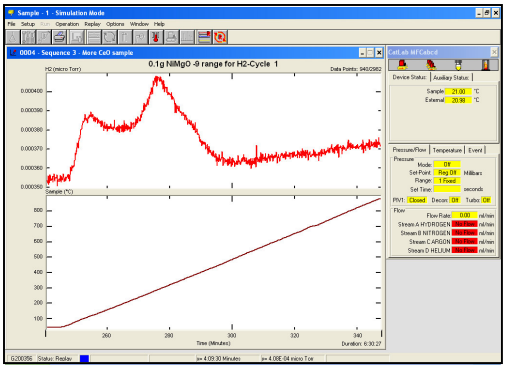

Figure 2 H_2 TPD from a NiMgO Catalyst

TPRx

TPRx is closely related to TPD but entails either the co-adsorption of species or a carrier gas containing the reagents is passed over the catalyst enabling the monitoring their interactions and reactions on the surface. In both cases a linear temperature ramp is applied to the sample. This approach allows kinetic parameters and activity studies over the selected temperature range to be performed and also allows information such as optimum reaction temperature to be evaluated. These techniques can also be used to perform deactivation studies and provides information on reaction mechanisms.

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 per second on a site) or a high selectivity with respect to 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.