

Temperature-Programmed Reduction of Platinum Group Metals Catalysts

RECENT TRENDS IN CHARACTERISATION TECHNIQUES

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The characterisation of platinum group metals catalysts is commonly carried out by temperature-programmed reduction, the spectrum of which has been used as a "finger-print" of the reducibility of the catalyst. Recent literature suggests that the utility of temperature-programmed reduction can be further enhanced by combining it with other techniques, such as temperature-programmed desorption and thermogravimetry. Temperature-programmed reduction can be used to investigate phenomena such as metal-support interaction and bimetal formation qualitatively, and to assess quantitatively the stoichiometry of the catalytic precursor. It may also be used to assess metal distribution in a composite oxide supported precursor. An overview of the concepts and applications of temperature-programmed reduction is presented here, and a selection of recent reported methodologies and findings on supported platinum group metal catalysts are discussed.

Catalyst characterisation techniques may be classified into physical methods and chemical methods. Among the latter, temperature programmed reduction (TPRd) is popular because of its low cost, relatively simple instrumentation, and utility. It can be used to provide qualitative as well as quantitative information on noble metal catalysts. Recently, it has been shown that the potential of TPRd as a catalyst characterisation tool can be enhanced by combining it with other techniques such as temperature-programmed desorption (TPD) and thermogravimetry (TG).

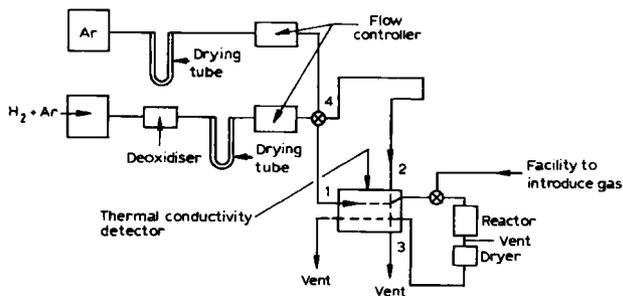
The theoretical considerations involved in TPRd are discussed first, then specific examples are provided to illustrate the applications of TPRd in the characterisation of noble metal catalysts.

During temperature-programmed reduction the composition of the gas flowing over the catalytic precursor is monitored during a well-defined temperature change, which is usually linear in time. In this paper, the term catalytic

precursor is used to refer to the entity before reduction; the material obtained after reduction is designated the catalyst. The reduced entity may not necessarily possess the catalytically active site, and the oxidation state of the active site depends on the nature of the reaction. A thermal conductivity detector is generally used to assess the gas composition. A thorough review of the apparatus and the principles involved in TPRd has appeared in the literature (1).

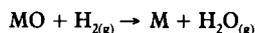
The results in a TPRd experiment are obtained as a trace of the thermal conductivity detector response versus temperature. The position of the peak in the profile is determined by both the chemical nature and the environment of the reducible component, and the peak area reflects the amount of reductant, typically hydrogen, consumed. Experimental parameters such as heating rate and gas flow rate affect the sensitivity of the technique (2). The peaks usually become sharper with an increase in the heating rate and a decrease in

Fig. 1 This schematic diagram of the TPRd/TPD apparatus indicates how the hydrogen/argon and argon gas streams can be directed to the reactor through the four-way valve: 1 carrier gas inlet, 2 sample gas inlet, 3 sample gas outlet, 4 four-way valve



the carrier gas flow rate. Also, the reduction peak shifts to a higher temperature when the heating rate increases. TPRd experiments may be conducted at several heating rates to calculate the activation energy of the reduction process. Typically, the peak temperature needs to be corrected for the time difference between the concentration and the temperature measurements.

The chemical reaction occurring during the TPRd process may be described by:



Reduction is feasible even when the standard free energy change for the above reaction is positive because the TPRd process is conducted in such a way that the product, water vapour, is consistently swept away from the reaction zone as soon as it is formed. The standard free energy changes associated with the reduction of metal oxides are listed elsewhere (1). These considerations apply even when the reducible species is a chloride, or an oxychloride, the only difference being that HCl is obtained as the reaction product.

Supported as well as unsupported catalytic precursors can be characterised by TPRd. Two models have been proposed for the reduction of unsupported precursors: the nucleation model and the contracting sphere model (1).

Such models, however, have limited applicability for studying the reduction of supported oxides where phenomena like adsorption, desorption, support reduction, hydrogen spillover and metal-support interactions affect the

hydrogen consumption observed. A procedure has been proposed to assess the adsorption and desorption components in a TPRd spectrum quantitatively (3). This involves the use of several TPRds and cooling cycles in an inert gas such as argon. The difference between the spectra observed during successive cycles is used to determine the adsorption/desorption component.

Temperature-programmed desorption can be easily combined with a TPRd experiment because of the similarities of the procedures. In the former the desorption of gases from a catalyst surface is monitored when it is heated in an inert gas stream; an in-depth review of TPD has appeared previously (4). A TPRd apparatus may be used to conduct TPD studies, and a schematic diagram of a typical TPRd apparatus is shown in Figure 1. Following a TPRd step, a gas such as hydrogen is adsorbed on the surface of the metal at an appropriate temperature, usually by pulse injections of hydrogen into the carrier gas stream upstream of the reactor. The temperature of the catalyst is increased linearly with time; the desorption rate increases with temperature, goes through a maximum, and eventually drops back to zero when the surface is depleted of the adsorbate. The TPD spectrum is a record of the concentration of the desorbed gas versus temperature, while the shape and position of the peak are related to the heterogeneity of sites and the chemisorption strength of the adsorbed component. The integrated area under the TPD peak thus

corresponds to the amount of the hydrogen adsorbed.

Although a thermal conductivity detector is commonly used to determine the composition of the gas during a TPRd experiment, the reduction process may also be followed gravimetrically by monitoring the weight of the catalytic precursor using a microbalance, that is by thermogravimetry (TG).

Temperature-Programmed Reduction Applications

The trace generated from TPRd is a "fingerprint" of the catalyst. Traditionally, the TPRd technique has been applied to the study of the influence of support materials (5), pretreatment procedures (6) and promoters on the reducibility of the catalyst surface (7). The peak temperatures observed during TPRd may be indicative of different phenomena. TPRd has been used to investigate processes such as the reduction of particulate and dispersed phases of the noble metal (8, 9), decomposition of metal hydrides (10), removal of surface species (11) formation of non-stoichiometric entities due to support reduction (11), and formation of mixed metal oxides (11).

Recently, it has been shown that TPRd may be used qualitatively to investigate phenomena such as metal-support interactions (12) and bimetal formation (13). It can be used in conjunction with TPD to study the Strong Metal Support Interaction phenomenon (14); TPRd results and those from TG results can be used to assess quantitatively the stoichiometry of the catalytic precursors and the extent of support reduction (12). It may also be used to assess the distribution of the metal in a composite oxide supported catalyst (15). The methodologies and recently reported findings are discussed in the next sections.

Metal-Support Interactions

Peak temperatures observed during the reduction of unsupported compounds and supported precursors have been used to assess the strength of metal-support interactions

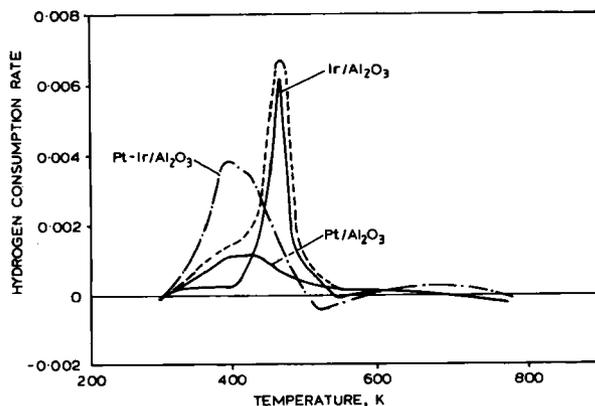
(16). It has been proposed that higher reduction peak temperatures are indicative of stronger metal-support interactions. Similar studies conducted on supported platinum precursors have shown that the strength of the platinum-support interactions varies as $\text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{TiO}_2$ (12).

Another type of interaction that occurs in supported catalysts is the formation of a support over-layer, such as TiO_x , which spreads over the surface of the noble metal. This phenomenon is commonly referred to as the Strong Metal-Support Interaction (SMSI) (17). The formation of the support over-layer suppresses chemisorption of gases such as hydrogen. Since the over-layer formation occurs in a reducing environment, the reduction of supported precursors at high temperature results in suppressed hydrogen chemisorption. TPRd/TPD experimental sequences have been used to investigate the SMSI phenomenon in TiO_2 -supported platinum and iridium catalysts (14). The amount of hydrogen desorbed during TPD is quantitatively determined and this provides a measure of the exposed metal surface area. The extent of suppression in hydrogen chemisorption increases with the reduction temperature and the number of times the TPRd step is performed. The TPRd/TPD sequence can be repeated several times and the amount of hydrogen desorbed during TPD can be used as a measure of the propensity for over-layer formation.

Bimetal Formation

The term bimetal refers to clusters of two metals, such as platinum-iridium or platinum-rhenium, having a relatively large surface area. Such entities may be prepared by sequential impregnation or by co-impregnation, and their formation can be studied using TPRd. The TPRd traces for Al_2O_3 -supported platinum, iridium, and platinum-iridium precursors are shown in Figure 2 (13). The appearance of a peak not seen in the monometal systems has been used as a measure of bimetal formation. Another indication of bimetal formation that applies to the

Fig. 2 These TPRd profiles for Pt/Al₂O₃, Ir/Al₂O₃ and Pt-Ir/Al₂O₃ precursors plot hydrogen consumption rates (in arbitrary units) against temperatures, so indicating bimetal formation. Reprinted from (12), with permission

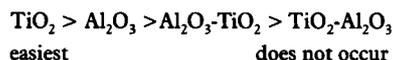


platinum-iridium system is the appearance/disappearance of the IrO₂ peak. It is known that the oxidative agglomeration of iridium to form IrO₂ is inhibited by platinum-iridium bimetal formation (18). Therefore the disappearance of the IrO₂ peak in the reduction profile can be used to identify bimetal formation.

The line for platinum-iridium/alumina in Figure 2 is clearly different from that obtained by adding together the spectra observed for the iridium (IrO₂ peak) and platinum precursors (the unlabelled broken line). Likewise, the IrO₂ peak is not observed in the case of the platinum-iridium/alumina precursor.

The effect of the support composition on the bimetal formation process can be studied using TPRd. The platinum-iridium bimetal formation in Al₂O₃, Al₂O₃-TiO₂, TiO₂-Al₂O₃,

and TiO₂ precursors has been investigated (13). This study shows that the use of composite oxides inhibits bimetal formation. It has been proposed that the ease of bimetal formation varies as:

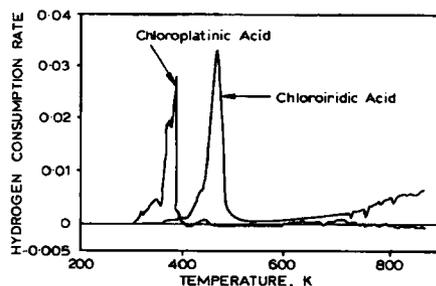


The TPRd/TPD experiments conducted in this study also indicate that Pt-Ir/TiO₂ catalysts show less tendency for TiO_x formation than both the TiO₂-supported platinum and iridium catalysts.

Stoichiometry of Catalytic Precursors

In a typical catalyst preparation sequence, the precursor is dried before calcination. TPRd can be used in conjunction with TG to

Fig. 3 TPRd of bulk chloroplatinic acid and chloroiridic acid, plotting hydrogen consumption rates (arbitrary units) against temperatures. Reprinted from (12), with permission



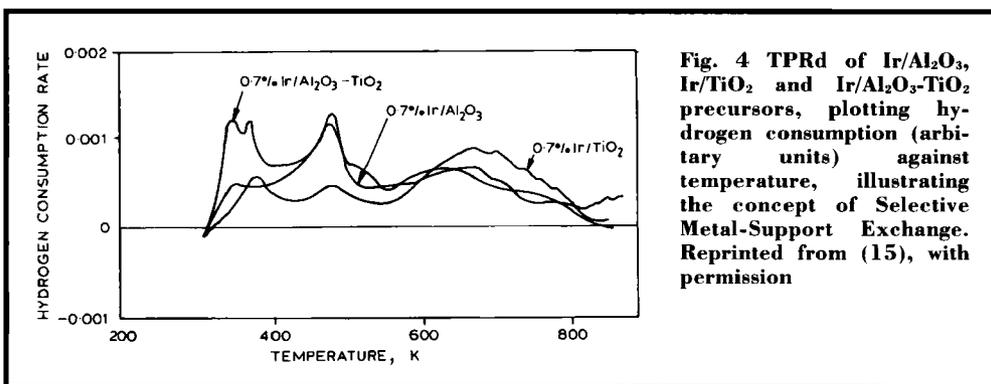


Fig. 4 TPRd of Ir/Al₂O₃, Ir/TiO₂ and Ir/Al₂O₃-TiO₂ precursors, plotting hydrogen consumption (arbitrary units) against temperature, illustrating the concept of Selective Metal-Support Exchange. Reprinted from (15), with permission

assess the stoichiometry of supported noble metal precursors after drying. The reductions of the supported precursor and of the support contribute to the hydrogen consumption observed during TPRd of a supported noble metal precursor. Likewise, the above processes also contribute to the weight loss observed during TG. The TPRd and TG data may be analysed by an iterative procedure to determine the stoichiometry of the precursor before reduction. The detailed description of this procedure has been reported elsewhere (12).

Recent studies have shown that PtCl₄ and IrCl₃ are formed on the Al₂O₃ and TiO₂ surfaces when Al₂O₃ and TiO₂ supported H₂PtCl₆ and H₂IrCl₆ are dried at 150°C. Temperature-programmed reduction may also be used to study the decomposition of bulk compounds such as chloroplatinic and chloroiridic acid, see Figure 3. The spectra show that the reduction of H₂PtCl₆ is a multi-step process whereas the decomposition of H₂IrCl₆ is seen to be a single step process.

Distribution of Noble Metals in a Composite Oxide Catalyst

Surface charge considerations suggest that the metal ions (from solution) may be exchanged selectively on one of the components of the composite oxide. This is called Selective Metal Support Exchange (SMSE) (19). TPRd has been used to identify the metal-support combination and thereby assess the distribution of the noble metal species in composite

oxide supported catalysts (15). The TPRd spectra for the Al₂O₃, TiO₂, and Al₂O₃-TiO₂ supported iridium precursors are shown in Figure 4.

The comparison of reduction peak temperatures for the iridium species distributed on the pure Al₂O₃ and TiO₂ supports with those observed during the reduction of a Ir/Al₂O₃-TiO₂ precursor suggests that iridium is selectively distributed on the Al₂O₃ when Al₂O₃-TiO₂ is used as the support. In the case of the Pd/SiO₂-Al₂O₃ the distribution of palladium on SiO₂ and Al₂O₃ has been quantitatively determined using TPRd (20).

Concluding Remarks

Temperature-programmed reduction (TPRd) has conventionally been used as a qualitative tool in studying the reducibility of the catalytic precursors. Recent literature suggests, however, that the utility of TPRd as a catalyst characterisation tool can be enhanced by combining it with other techniques such as temperature-programmed desorption and thermogravimetry. Phenomena such as bimetal formation, Strong-Metal Support Interaction, and Selective Metal-Support Exchange can all be investigated using TPRd, which can be used in conjunction with TG to determine quantitatively the stoichiometry of the catalytic precursor.

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Iridium Protects Rocket Thrusters

The efficiency of spacecraft thruster engines, used for orbit insertion and altitude control, will be improved if their operating temperatures can be increased. As the fuel comprises the bulk of the mass of a satellite any reduction in requirement permits an increase in payload and hence an enhancement of the mission. The limitation on the efficiency of rocket engines may, however, be the ability of the materials they are made from to withstand the arduous conditions encountered in service.

Materials for radiation-cooled rocket thrusters must be capable of providing both mechanical strength and oxidation resistance at the high operating temperatures demanded by engine efficiency, but no single material has the necessary combination of properties. Rhenium, with a melting point of 3180°C, has suitable mechanical properties but under the oxidising conditions encountered in thruster chambers rapid loss of material occurs. This can be prevented by coating the surface of the rhenium which will be exposed to hot combustion gases with iridium. This does not form a eutectic with rhenium, has suitable thermal expansion and is reasonably resistant to oxidation at temperatures up to 2410°C – its melting point.

In order to be able to predict the lifetime of iridium-coated rhenium thrusters investigators with the Sandia National Laboratories, Livermore, and with the Aerojet Propulsion Division, Sacramento, have studied samples cut

from a thruster end ring. This had been manufactured by chemical vapour deposition, involving the deposition onto a molybdenum mandrel of a layer of iridium approximately 50µm thick which was then overlain with 2 mm of rhenium before the molybdenum was removed by chemical etching. As deposition of the rhenium takes place at 1200°C some interaction takes place during this process. It is suggested that failure of such components could involve the diffusion of rhenium through the iridium and the subsequent removal of rhenium by oxidation; hence the need for accurate diffusion data. ("Diffusion Mechanisms in Chemical Vapor-Deposited Iridium Coated on Chemical Vapor-Deposited Rhenium", J. C. Hamilton, N. Y. C. Yang, W. M. Clift, D. R. Boehme, K. F. McCarty and J. E. Franklin, *Met. Trans.*, 1992, **23A**, (3), 851–855).

Diffusion mechanisms and rates are critically affected by the grain size and morphology of the materials, and these were determined by electron microprobe analysis of a control sample and three others which had been annealed in vacuum for specified times at temperatures slightly below rocket thruster operating temperatures.

The evidence showed that for these chemical vapour-deposited materials grain-boundary diffusion was the dominant diffusion mechanism and the diffusion rate showed an Arrhenius-type dependence on temperature, enabling operating lifetimes to be predicted.