



Evaluation of Metal Reduction Catalysts

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ABSTRACT

Evaluation of precious metal reduction catalysts is normally a time-consuming process. Pressure differential scanning calorimetry (PDSC) provides a much faster alternative for scanning these materials.

INTRODUCTION

The efficient reduction of numerous organic compounds depends upon the activity of precious metal catalysts such as platinum and palladium. These metals are normally deposited on inert, porous substrates, such as carbon or silica. Catalyst activities are generally evaluated by one or both of two methods. The first method measures the volume of hydrogen absorbed by the catalyst under pressure as an indication of the active site availability. The second method measures the volume of hydrogen consumed during the reduction of a test compound added to the catalyst. Both methods require six hours or longer and use large samples in a pressure autoclave. They are therefore time-consuming, expensive and potentially hazardous to personnel and equipment.

Chemisorption and catalytic reduction are both exothermic reactions, with the heat evolved being directly related to the hydrogen consumed. Therefore, thermal analysis techniques, particularly differential scanning calorimetry (DSC) offer a viable alternative to autoclave techniques. The TA Instruments Pressure DSC (PDSC) cell, usable to 7.0 MPa (1000 psig), is particularly amenable to such studies. Using increased pressure of hydrogen, a PDSC reduction can be completed in 15 minutes or less. This means that about 20 samples can be evaluated in the same time normally required to test only one in an autoclave. This dramatic decrease in analysis times make the screening of each catalyst batch economically feasible.

EXPERIMENTAL

Differential scanning calorimetry measures the difference in heat flow between a sample and an inert reference as they are subjected to heating or cooling in a controlled atmosphere. The resulting heat flow is measured by highly sensitive area thermocouples and used to determine temperatures of transitions (*e.g.*, melting point), as well as heats of reaction. In most DSC experiments, the atmosphere around the sample is a flowing purge gas (usually air or nitrogen) at atmospheric pressure. In PDSC, the choice of viable atmosphere gases is generally the same as in conventional DSC, but the pressure of the

purge gas (atmosphere) becomes an additional experimental variable. Increasing pressure of the purge gas has two primary benefits - suppression of pressure sensitive reactions (*e.g.*, volatilization) and acceleration of sample-atmosphere reactions (*e.g.*, oxidation, catalytic reduction). In each case, the presence of higher concentration of the reactive gas accelerates the reaction for rapid screening or comparison of materials.

In this case, a series of precious metal reduction catalysis were evaluated under hydrogen at a gauge pressure of 1.4 MPa (200 psig). 5 mg (nominal) of catalyst were placed in an open aluminum sample pan and loaded into the PDSC at room temperature. The cell was closed, flushed several times with helium at 350 kPa gauge pressure (50 psig), and then pressurized to 1.0 MPa gauge pressure (150 psig) before initiating of heating at 20 °C/min. When the sample temperature reaches 75 °C, the purge gas is switch from helium to hydrogen at 1.4 MPa gauge pressure (200 psig).

RESULTS

Figure 1 shows a typical DSC curve obtained. An initial endothermic event occurs when the gas is switched, followed by a large exothermic peak due to the chemisorption reaction. The PdO/Carbon catalyst shown in Figure 1 was run six times with an average heat of reaction of 81.6 ± 1.0 J/g (1.3 % RSD). No attempt was made in this procedure to calculate adsorption on the carbon, and in fact, the shoulder on the leading edge of the exothermic peak is due to the physical adsorption on the carbon.

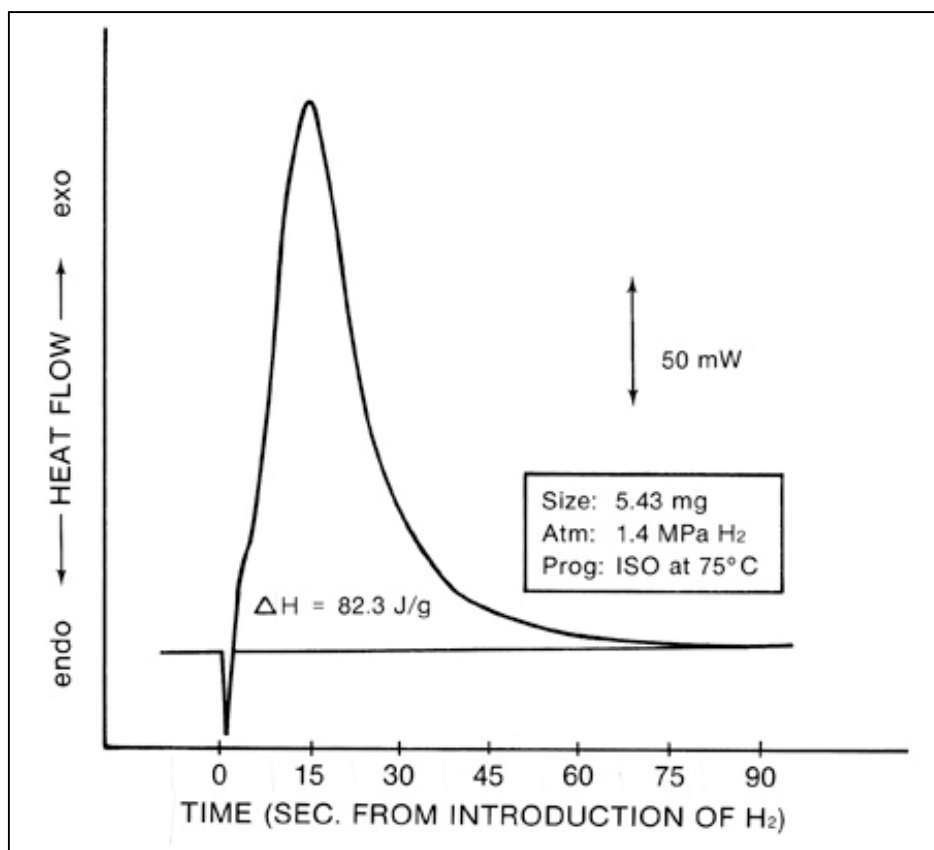


Figure 1 - Hydrogen Adsorption onto PdO/Carbon Catalyst

The heats of reaction for this series of commercial catalysts are shown in Table 1. The heats of chemisorption cannot be compared between metals on different substrates without first correction for the heat of physical adsorption on the substrate. Furthermore, the relative activities of catalyst systems for a specific hydrogenation process cannot be predicted from the heats of chemisorption alone because of substrate differences. Different substrates reflect differences in structure, surface area, pore size, pore volume, *etc.* that, in turn, affect catalyst metal surface area plus catalyst metal distribution on the substrate. Nevertheless, it is interesting to note that the order of activity observed in chemical reductions using these catalysts agrees with the PDSC results. For example, Pd is generally more reactive than Pt and carbon is a more reactive substrate than alumina.

An extension of these procedures can be used to evaluate mixed metal catalyst, for example Pd-Pt catalysts where the loss of activity by the secondary metal can synergistically affect the total catalyst activity (1, 2). In addition, PDSC can be used, via a similar procedure, to evaluate catalyst activity by reduction of an organic substrate such as m-dinitrobenzene (3). DSC (4, 5, 6) has also evaluated other types of catalyst system.

Table 1 - Evaluation of Catalyst Activities by PDSC

Catalyst	Activity (J/g)
5 % Pd/Carbon	81.6
5 % Pd/Calcium Carbonate	44.3
5 % Pd/Alumina	39.3
5 % Pt/Alumina	29.7
5 % Pt/Carbon	58.6
59 % Ruthenium Oxide	1247

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KEYWORDS

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