

Thermal Analysis Application Brief Evaluation of Metal Catalysts

Number TA-136

SUMMARY

Evaluation of precious metal reduction catalysts is normally a time-consuming process. Pressure differential scanning calorimetry (PDSC) provides a much faster alternative for scanning those 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 and silica. Catalyst activities are generally evaluated by one or both of two methods. The first measures the volume of hydrogen adsorbed by the catalysts under pressure as an indication of the active sites available. 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 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, which is usable to 1000 psig, is particularly amenable to such studies. Using increased pressures 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 time makes the screening of each catalyst batch economically feasible.

EXPERIMENTAL

Differential scanning calorimetry measures the differential 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 (eg. melting point), as well as heats of reaction. In most DSC experiments, the atmosphere around the sample is flowing purge gas (usually air or nitrogen) at atmospheric pressure. In pressure DSC, the atmospheric options are the same as in conventional DSC, with regard to the choice of viable gases, 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 (eg. volatilization) and acceleration of sample-atmosphere reactions (eg. oxidation, catalytic reduction). In the latter cases, 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 catalysts were evaluated under hydrogen at 200 psig. 5mg (nominal) of catalyst was 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 50 psig, and then pressurized to 150 psig before initiation of heating at 20°C/minute. When the sample temperature reached 75°C, the purge gas was switched from helium to hydrogen at 200 psig.

RESULTS

Figure 1 shows a typical DSC curve obtained, an initial endothermic blip 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 19.5 ± 0.25 kcal/mg (1.25% rel.). No attempt was made in this procedure to calculate separately the heat of chemisorption and that of physical 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.



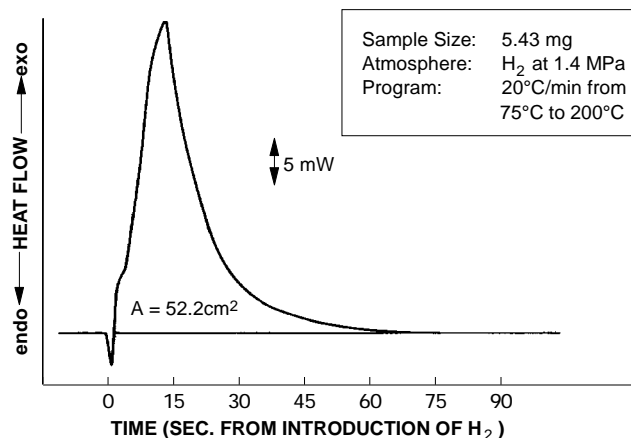
The heats of reaction for this series of commercial catalysts are shown in Table 1. The heats of chemisorption cannot be compared between metals on different substrates without first correcting for the heat of physical adsorption on the substrate. Furthermore, the relative activities of catalyst systems 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. which, 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 this procedure can be used to evaluate mixed metal catalysts, 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). Other types of catalyst systems have also been evaluated by DSC (4, 5, 6).

TABLE 1

EVALUATION OF CATALYST
ACTIVITIES BY PDSC

	mcal/mg
5% Pd/Carbon	19.5
5% Pd/Calcium Carbonate	10.6
5% Pd/Alumina	9.4
5% Pt/Alumina	7.1
5% Pt/Carbon	14.0
59% Ruthenium Oxide	298.0



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