

**Benson J E & Boudart M.** Hydrogen-oxygen titration method for the measurement of supported platinum surface areas.  
*J. Catalysis* 4: 704-10, 1965

This paper describes the development of a new method for determining the degree of dispersion of platinum in supported catalysts. The method relies on the fact that chemisorbed oxygen on platinum can be titrated off quantitatively by dihydrogen at room temperature. To count surface platinum atoms all that is needed is to know how many oxygen atoms per platinum atom are replaced by how many hydrogen atoms per platinum atoms. [The *SC*<sup>®</sup> indicates that this paper has been cited over 135 times since 1965.]

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"In the Fall of 1955 I made a trip to Penn State, my alma mater, from Princeton where I was just completing my Ph. D. During my visit I learned of research, under the direction of Professor J.G. Aston, which had as its objective the calorimetric determination of the heats of chemisorption of dihydrogen oxygen. Later, in 1960, this research was reported in full at the Second Meeting of the International Congress on Catalysis in Paris.<sup>1</sup>

"In 1964 I joined the group at Stanford University headed by my former Princeton colleague, Professor Michael Boudart, for a sabbatical year. He suggested to me that we might use the idea of Aston to develop a method for counting the number of surface platinum atoms in supported catalysts and thus determining the efficiency with which the expensive and rare metal had been laid down on the support. The idea was really very simple: if we chemisorbed oxygen on hydrogen-reduced and outgassed platinum and then allowed this chemisorbed oxygen to react with dihydrogen in the gas phase, the water formed would be taken up by the hydrophilic support, alumina. Thus, the decrease in the number of dihydrogen molecules in the gas phase would count the number of surface platinum atoms.

"It should be pointed out that the BET method for determining surface area, an invaluable tool for unsupported metals, will not work for supported metals since it is not selective for the metal alone.

"In the method proposed by Boudart, the reaction is selective and would have the further advantage of being three times as sensitive as chemisorption of dihydrogen since three hydrogen atoms are consumed for each surface platinum atom instead of one.

"After the construction of a standard adsorption apparatus in a crowded, dingy and sometimes rain-flooded building, now replaced by a modern laboratory, it was a simple matter to take the data and check the method

"In the early stages of the research erratic data were obtained, and I could not pinpoint the reason until one day when I noticed that the Pyrex glass wool used to hold the finely powdered samples in place was turning grey when it was heated. I packed some wool in a tube, passed clean air through it and, sure enough, it turned grey and smelled oily. Only then did I realize that the wool was coated with oil which, upon oxidation, could absorb dihydrogen. Subsequently, we used only wool that had been boiled in concentrated nitric acid

"Another discovery was that it was possible to extrapolate the isotherms to zero pressure to wipe out the contribution of physical adsorption on the support. As a result we were able to measure the titration of oxygen atoms by dihydrogen on the metallic platinum.

"Of considerable help to us during the developmental stages of our work was the cooperation of Dr. T. R. Hughes, then at California Research Corporation. He and his colleagues prepared some catalysts and characterized them by CO adsorption. The results were compared with our results on the same samples and were gratifyingly consistent in the trend in dispersion.

"A major worry was that we had no knowledge of the stoichiometry of the three reactions involved: the chemisorption of dihydrogen and dioxygen on platinum and the reaction of dihydrogen with chemisorbed oxygen. We attempted to answer this question in our paper, but this question persisted and has led to many papers. It is because of this question that our paper has been cited so many times. I feel that the major contribution is that we have stimulated a great deal of research in trying to understand these simple reactions. Besides, the method has been used extensively all over the world in theoretical and practical catalytic studies.

## REFERENCE

1. Chon I H, Fisher R A, Tomeszko E & Aston J G. Chemisorption of hydrogen and oxygen on platinum black at low temperatures. *Actes du Deuxieme Congres International de Catalyse*. 2<sup>e</sup>. 1960, Paris. Paris: Editions Technip. 1961. p. 217-26.