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TRUE DIFFERENTIAL MICROCALORIMETRIC STUDY OF THE STRUCTURE OF BIMETALLIC CATALYST PARTICLES

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ABSTRACT

A Calvet-type true differential microcalorimeter was used to study the surface chemistry of graphite-supported Fe/Rh catalyst particles. The calorimeter has some novel features, including the capability of measuring the kinetics of adsorption of each "differential" gas dose. Previous work indicates that the structure of Fe/Rh particles changes dramatically as a function of treatment. Indeed, recently it was suggested that; (i) following oxidation (200°C) metal segregation takes place within the particles such that iron-oxide and rhodium-oxide zones exist within each particle; (ii) hydrogen treatment at low temperature (100°C) results in the reduction of these zones without alloy formation; and (iii) only hydrogen treatment at high temperature (400°C) leads to alloy formation. In this study, the calorimeter was used to measure the adsorption of oxygen on the supported metal particles in each of the reduced-metal "structures" described above. The data strongly supports the above model.

INTRODUCTION

Supported bimetallic particles have attracted much attention in the catalytic literature due to their interesting properties. Several years ago, Sinfelt demonstrated that a catalyst composed of small supported bimetallic crystallites exhibited activity and/or selectivity which differed significantly from that of either of the individual metal components [1]. Hence, many workers have attempted to determine the metal phases which exist in bimetallic systems and to correlate this to the interesting chemical behavior [2].

In a recent article [3], a model was proposed to explain the

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phase behavior of graphite-supported Fe/Rh crystallites. A schematic of the structural dynamics is presented in Figure 1. As is shown, three or four distinct "states" of the catalyst can be achieved by different gas-temperature treatments. In particular, two distinct types of fully-reduced metal particles are possible: FeRh-alloy (following 400°C hydrogen reduction) and segregated α-Fe and τ-Rh (following 200°C oxidation and 100°C hydrogen reduction). The present work examined the surface chemistry of these different structures, using a novel adsorption microcalorimeter designed in our laboratory.

EXPERIMENTAL

Differential Adsorption Microcalorimeter. In order to obtain a detailed profile of the nature and distribution of surface sites on this supported-metal catalyst system, an innovative differential microcalorimeter was designed which measures the true differential heat of adsorption of gases on the surface of the particles as a function of gas coverage. The

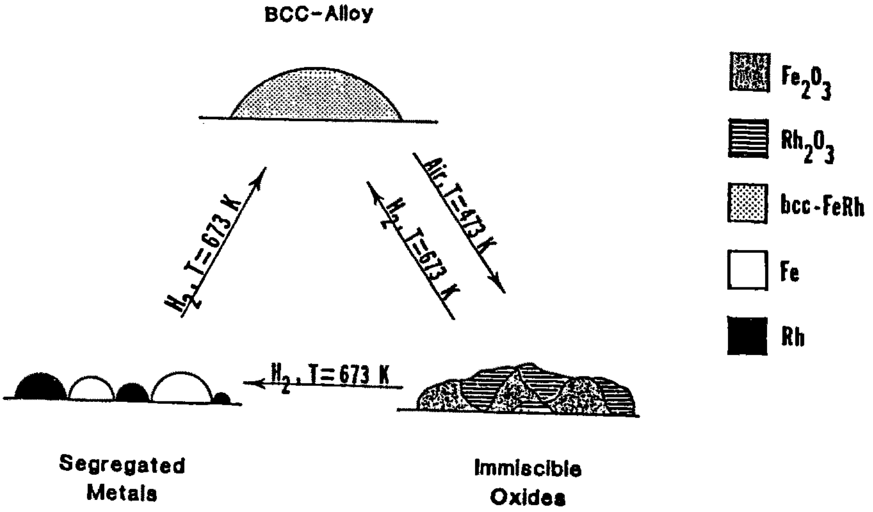

Figure 1. Proposed model of graphite-supported FeRh particle dynamics as a function of oxidation/reduction.

system is of the Calvet heat-flow type [4], but is modified to allow simultaneous measurement of both adsorption kinetics and heat evolution dynamics. A schematic of the instrument is given in Figure 2. The sample cell, a hollow glass disk, is "sandwiched" between commercially available thermopile sheets and large aluminum blocks which act as a constant temperature heat sink (Figure 2.a). When gas is admitted into the sample bed, heat is evolved, establishes a temperature gradient between the bed and the heat sink, and then flows through the thermopiles, which produce a voltage signal that is directly proportional to the amount of heat flowing through them. By integration of the resulting thermogram, the total amount of heat evolved during the dose can be obtained [5]. Figure 3.a shows typical thermograms for various stages of a chemical adsorption experiment.

The gas uptake is measured volumetrically by Baratron Capacitance Manometers (MKS Instruments, Inc.) which have been incorporated into the dosing volume (see Figure 2.b). In this way, dynamic pressure changes can be monitored throughout the adsorption process. Both qualitative and quantitative information are available from a plot of the pressure response. Figure 3.b shows some typical pressure response curves corresponding to the thermograms plotted in Figure 3.a.

Catalyst Samples. The catalyst samples consisted of small crystallites (ca. 200 A in diameter) of Fe, Rh or FeRh supported on an inert graphitic substrate (GTA-Grade Grafoil, Union Carbide Corp.). The samples were prepared by the incipient wetness technique using aqueous solutions of the the monometallic salts ($Fe(NO)_3$ and $RhCl_3$) for the two monometallic catalysts, and an organic solution of a bimetallic FeRh carbonyl derivative $[(CO)_3Fe(C_7H_7)Rh(C_8H_{12})]$ [6] for the bimetallic catalyst. Metal loadings for the three samples were approximately 5 percent by weight. Except where indicated, the samples were typically reduced in hydrogen at 400°C, evacuated at 400°C to 1×10^{-5} torr, and then cooled to 30°C and transferred to the sample cell for the adsorption experiment. The data presented in the following section are from oxygen adsorption experiments at 30°C.

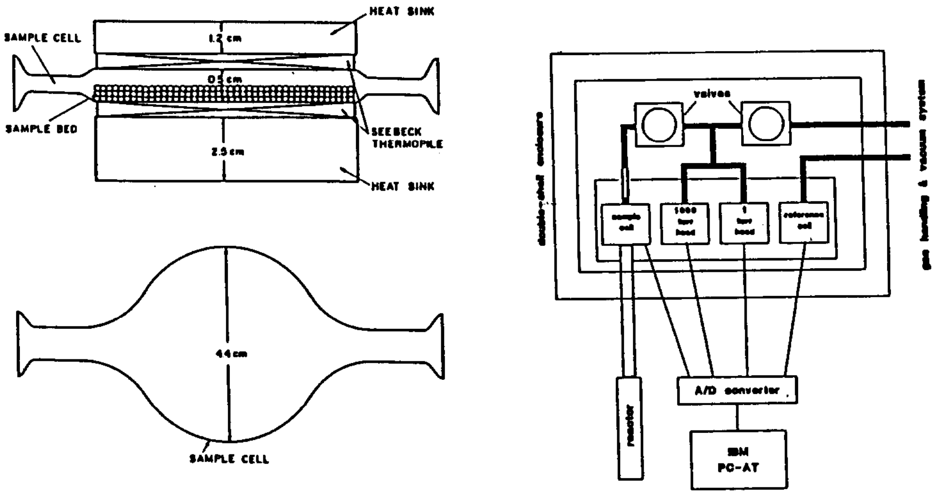

Figure 2. Differential Adsorption Microcalorimeter. (a) Sample cell and thermopiles; (b) Overhead view.

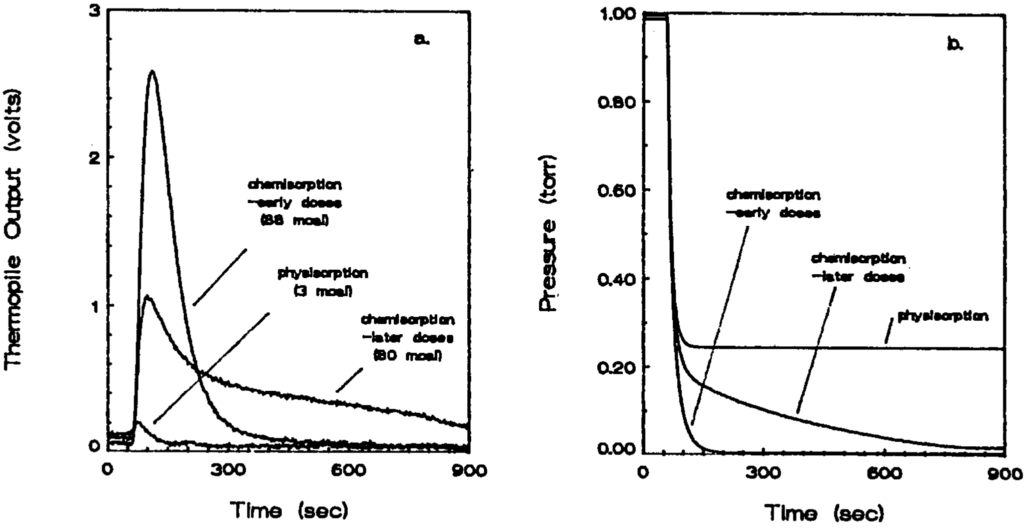

Figure 3. Typical chemisorption experimental data. (a) Heat-flow thermograms and (b) Pressure-response curves.

RESULTS AND DISCUSSION

Differential heat of adsorption data are given in Figure 4.a for room-temperature oxygen adsorption on monometallic Fe, monometallic Rh, and bimetallic FeRh catalyst samples. In this figure, the data have been normalized so that the total amount of chemisorbed oxygen corresponds to a fractional coverage of 1.0. The data clearly show that oxygen adsorption on iron is a steady, high-heat process through a coverage of approximately 0.75. After this point, the adsorption process slows significantly, and the heats rapidly fall off until the surface is completely passivated, and only physical adsorption is occurring [7]. In contrast, the heats of adsorption of oxygen on rhodium are seen to steadily decrease from the start. This decrease becomes more rapid after a coverage of approximately 0.6, at which point the adsorption slows dramatically with each successive dose until the physical adsorption point is reached. The heats of oxygen adsorption on the fully-reduced (400°C) bimetallic catalyst (BCC-FeRh alloy) sample fall between the two monometallic extremes

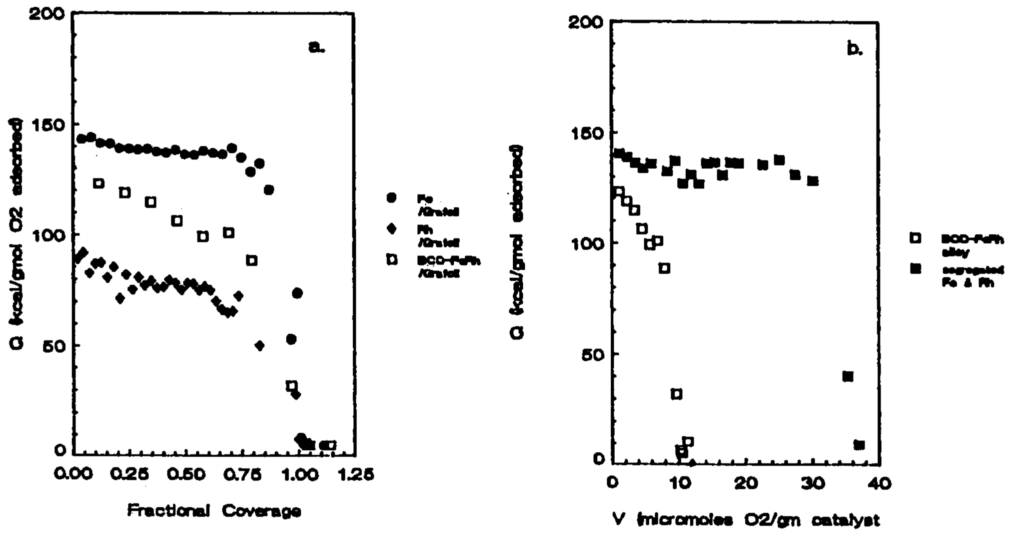

Figure 4. Differential Heat of Oxygen Adsorption at 303 K. (a) Comparison between supported Fe, Rh and FeRh; (b) Comparison between alloyed and segregated FeRh.

throughout the coverage range. The heats are initially high, close to that of iron, and fall off steadily until the surface is covered with a chemisorbed layer. The data of Figure 4.a are clearly the result of adsorption on a bimetallic alloy surface. The initial iron-like heats are reasonable, since oxygen is expected to preferentially adsorb on iron sites at low coverages due to the high heats associated with Fe-O bond formation. As coverage increases, the heats fall off as the rhodium sites become progressively more important. This behavior consistent with models of oxidation of bimetallic alloys consisting of iron and a noble metal [8].

Figure 4.b presents the data from oxygen adsorption on the bimetallc catalyst in its two "reduced states", as indicated in Figure 1. The adsorption behavior of the sample after 200°C oxidation and subsequent 100°C reduction is dramatically different from that of the alloy. First, the initial heats are higher, and remain high to much higher coverages. This behavior is much more iron-like than that of the alloy. Second, the total coverage is nearly four times that of the alloy phase. This may be explained by either an increase in the metal surface area, or a change in the adsorption stoichiometry. In either case, the data supports the segregation model presented in Figure 1.

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