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Effect of oxygen on the production of abnormally high heats of interaction with hydrogen chemisorbed on gold

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ABSTRACT

Abnormally high heats, exceeding 1600 kJ/mol (16 eV) per molecular oxygen, are generated by interaction of the oxygen with the hydrogen adsorbed on gold surfaces at 125 °C. The highest heats were observed during the interactions of fine gold particles supported on titanium oxide, approaching 1700 kJ/mol for three consecutive 100 nmol pulses of O_2 interacting with the adsorbed hydrogen atoms. The heats rapidly decrease after the hydrogen is consumed. It was also observed that the interactions of the gold particles with pure oxygen in the presence of noble gases, such as argon and helium, produced the heats markedly higher than those observed in the absence of noble gases. The abnormally high heats revealed by this work reach values from 3.5 to 6.1 times higher than the heats of formation of gaseous water from molecular hydrogen and oxygen.

1. Introduction

It is now firmly established that hydrogen is dissociatively adsorbed on gold particles deposited on various metal oxides and that the number of the chemisorbed hydrogen atoms increases with temperature and decreases with the increasing particle sizes [1]. It was also shown that there are differences in the binding strengths of the hydrogen atoms adsorbed on specific surface sites of the gold particles, related to the particle size. The weakly chemisorbed hydrogen was believed to be more active in reactions with other adsorbates, such as acetylene [1]. The strength of binding of the chemisorbed hydrogen atoms was calculated to be as high as -500 kJ/mol H_2 [2], which came close to the experimentally determined value of the heat of hydrogen adsorption on an Au/TiO_2 catalyst, using a flow-through microcalorimeter (FMC), which was -400 kJ/mol H_2 [3]. The latter heats could have been related not only to the reduction of Au^{3+} species [3], but also to changes in the length of Au–Au bonds observed after interactions of gold particles containing surface sites capable of strong interaction with hydrogen [2].

High heats of hydrogen adsorption on gold surfaces were also observed when a sample of pure gold powder was exposed to molecular oxygen after partial desorption of previously adsorbed helium and hydrogen. Sharp heat evolutions observed in this work reached values exceeding 800 kJ/mol O_2 after adsorption of 0.45 μmol of oxygen mixed in argon [4]. A real time graphical representation of this surprisingly high heat evolution is shown in Fig. 1. It became clear, therefore, that results of direct determination of the heats of interaction between the gold catalysts and oxygen could be related to high activity of hydrogen atoms adsorbed on the surfaces of gold particles and their performance in hydrogenation and oxidation reactions. Hence an important aspect of the activity of gold particles is the interaction of their surfaces with molecular oxygen.

It was reported recently by Heiz that dissociative adsorption of molecular oxygen occurs when it interacts with 20 atom gold clusters involving the formation of superoxo-states, but the energy of these interactions was not discussed [5]. However the energy of Au–O– bonds formed by dissociative adsorption of oxygen on the periphery of similar gold clusters was calculated by Pichugina and co-workers using the density functional theory with relativistic corrections. The calculated energies of bonds involved in the formation of O–Au–O and Au–O–O species were given as 15.6 kcal/mol and 62.7 kcal/mol (or 65.2 kJ/mol and 262 kJ/mol, respectively) for the facet gold atoms [6]. However the energy of the interactions between oxygen and gold surfaces containing chemisorbed hydrogen was not investigated.

In this paper the interactions between oxygen and the gold particles were examined before and after their exposures to hydrogen, using flow-through microcalorimetric methods. The work involved

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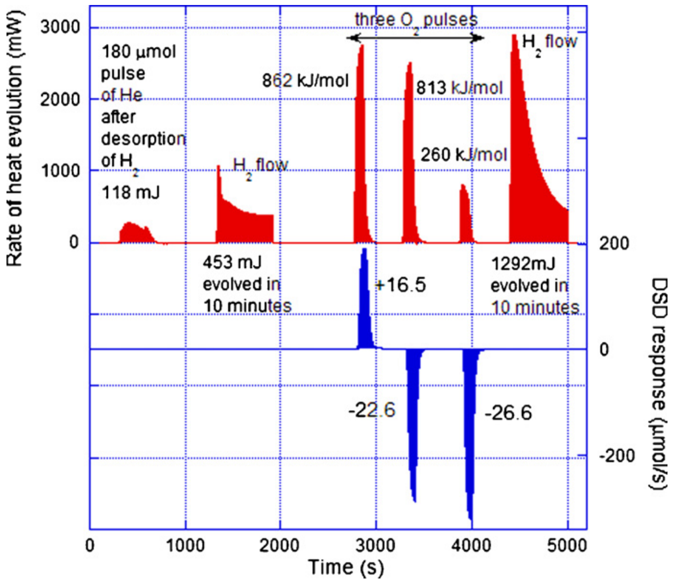

Fig. 1. Heat evolutions at 125 °C produced by sequential exposures of a 0.696 g sample of pure gold powder reduced with hydrogen at 220 °C. The sample was subsequently exposed at 125 °C to an 180 μmol pulse of helium followed by desorption with nitrogen flow and to tree pulses of 1% mixture of oxygen with argon each containing 0.45 μmol of oxygen. The first two pulses generated remarkably high heats of 847 kJ/mol and 809 kJ/mol. All the exposures were separated by brief periods of nitrogen flow. The argon component of the mixtures passed through the gold powder and generated a negative peak recorded by a TC detector, with the exception of the first oxygen interaction. The latter interaction produced a positive peak, which is normally recorded by the detector by hydrogen and helium and not argon which produces negative peaks. This suggests that the first interaction of the gold sample with oxygen involves desorption of the previously adsorbed He. In subsequent two oxygen pulses the argon diluent passes through the gold powder without any significant adsorption as indicated by the negative peaks recorded by the TC detector.

the interactions of oxygen with fine gold particles deposited on titanium oxide (1% Au/TiO$_2$ catalyst) that were reduced with hydrogen and then exposed to pulses of pure oxygen and 1% oxygen mixed with argon.

2. Experimental

2.1. Apparatus

Microscal flow-through microcalorimeter, model 4110 (FMC) was fitted with a ceramic calorimetric cell and stainless steel gas handling facilities. Thermal conductivity detector (TCD) monitored the composition of the effluent and flow rate was controlled by mass flow controllers. The microcalorimeter could be used at temperatures ranging from 20 °C to 240 °C and external pressures ranging from 1 bar/g to 50 bar/g. A detailed description of the microcalorimeter and its uses is described in a previous publication by the one of the authors [7].

An important feature in the FMC is an *in situ* calibration of the heat effects accomplished by an electrical coil (encapsulated in PTFE) situated in the centre of the cell in direct contact with the adsorbent. Heat effects obtained during the interactions of the adsorbent with reactants could thus be accurately calibrated under different conditions of gas flows, temperature and pressure.

In the present work the calorimeter was used isothermally at 125 °C at atmospheric pressure and gas flow rates of 1 cm^3/min.

2.2. Materials

All gases used in this work were supplied by Aldrich and had a purity of 99.999%. A sample of gold catalyst containing 1 wt% of gold supported on titanium oxide, as well as the pure TiO$_2$ support, was prepared and supplied by Prof. M.C. Scurrell.

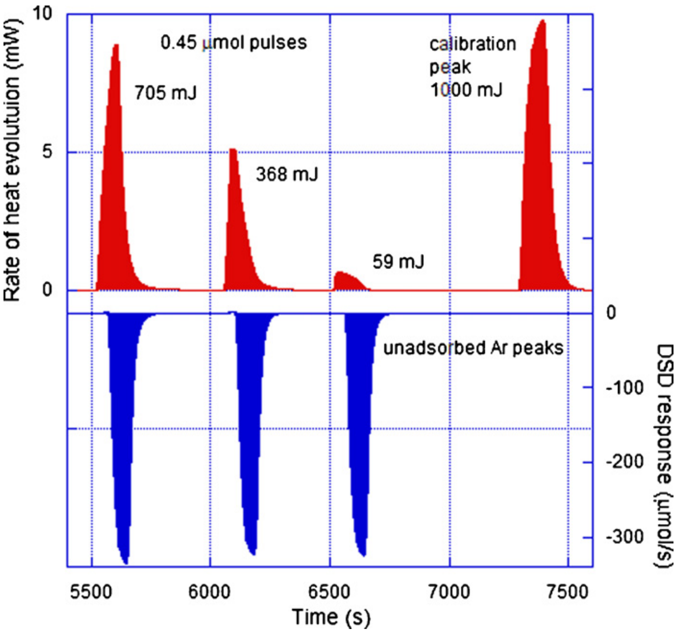

Fig. 2. Heat evolutions produced by the exposure at 125 °C of a sample of 0.083 g of 1% Au/TiO$_2$ catalyst to 0.45 pulses of oxygen in the form of 1% mixture with argon. The first peak represents heat evolved in about 250 s amounting to 705 mJ equivalent to 1567 kJ/mol. The last peak represents an electrical calibration generating 1000 mJ in 100 s.

2.3. Procedures

The calorimetric cell was filled with a powdered catalyst and sealed by top and bottom connections, the latter fitted with the calibration coil. The volume of the cell was 0.15 cm^3 and the adsorbent required to fill the cell was accurately weighed. Nitrogen, used as a carrier gas, was then passed via the top connection through the adsorbent sample at the rate of 1 cm^3/min at a temperature selected for the adsorption experiment. The temperature selected in this work was 125 °C. Initially the sample in the cell was purged by nitrogen flow for 20 h, which was sufficient to remove all the physically bound volatile impurities, including water, from the sample surfaces and to reach a stable thermal equilibrium. Adsorption and reaction experiments could then be performed by changing the flow of nitrogen to that of the reacting gases. The flows of the latter gases could be limited to small intervals of time resulting in relatively brief exposures of the adsorbents to the reactive gases (pulses). Alternatively, extended exposures lasting sufficiently long, sometimes as long as several hours, before complete saturation of the adsorbent surfaces could also be applied. Generally the adsorption was accompanied by the evolution of heat, an exotherm, which stopped when the adsorption was completed. The heat of desorption could be measured by changing the flow back to nitrogen causing desorption of the weakly adsorbed gas accompanied by heat absorption, an endotherm. Comparison of the exotherms with the endotherms served to establish reversibility of the adsorption processes.

3. Results and discussion

Heat evolution taking place when fine particles of gold deposited on titanium oxide (gold catalyst) are exposed to flow of pure hydrogen at 125 °C is represented graphically in Fig. 2. The catalyst consisted of 83 mg sample of 1 wt% of gold supported on TiO$_2$ and