STUDIES OF COMBUSTION RELATED SURFACE REACTIONS IN A COMBINED UHV-ATM PRESSURE EQUIPMENT

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Problem areas in combustion research where surface physics may have an impact are identified and discussed. An experimental system intended for fundamental studies of some of these problems is described. It consists of a conventional UHV system with an integral reaction cell for high pressure studies and for sample exchange. A progress report is given from studies of the influence of Si and O surface concentrations on the catalytic activity of polycrystalline Pt and from studies of the oxidation of thin C films.

1. Introduction

The purpose of this paper is threefold: (i) to present some of the questions in combustion research relating to surface physics, (ii) to describe an experimental set up intended for fundamental studies of such problems and (iii) to give a progress report from these studies.

The combustion of a gaseous air/fuel mixture is in principle a pure gas phase reaction. In practice, however, combustion takes place in the presence of solid surfaces that may influence the combustion process. In a combustion engine, for example, the cylinder walls and piston form a closed space in which a flame propagates, after the air/fuel mixture has been ignited. The outcome of the combustion process is then, among other things, governed by the boundary conditions set by the presence of the solid surfaces of the combustion volume. The boundary conditions are geometrical, thermal and chemical in nature since the solid surfaces determine how far the flame can propagate, the heat flow and temperature at the gas-solid interface, and the chemical processes at the interface, respectively.

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On a microscopic scale the combustion reaction is made up of a large number of unimolecular, bimolecular, or multimolecular collision events. Via reactive and inelastic collisions the reaction energy is distributed among the degrees of freedom of the reacting system (translational kinetic energy, rotations, vibrations and electronic excitations). This can be observed as a temperature rise of the system. Some of these processes also take place at the walls of the combustion chamber but at very different rates. The walls may also give rise to new processes such as radical recombination, neutralization of ions, de-excitation of excited species, etc. Very little is known about the relative importance (for the combustion process) of wall reactions, and possible coupling between homogeneous and heterogeneous reactions. The questions become particularly intriguing when catalytically active materials are present.

Different types of surface processes are associated with the soot particles that are always formed during combustion of hydrocarbons. The details about how they are formed are still the subject of much research and controversy, but there seems to be a whole spectrum of these so-called soot particles, ranging from essentially very unsaturated hydrocarbon molecules to carbon particles with a rather porous structure and a quite high content of hydrogen, but also with traces of many other elements (e.g. O, N and metals) [1]. During the combustion process soot particles are continuously formed and consumed (oxidized to CO and CO_2), and what comes out as soot in the exhaust may have physical and chemical properties quite different from the ones actually present during the combustion process.

Surfaces come into play in combustion also in several other ways. Catalytic cleaning of automotive exhaust gases (CO, NO_x , hydrocarbons, etc.) is a well known example. The surface properties of electrodes in fuel cells govern the catalytic processes in them and the electrode surfaces in spark plugs influence the ignition of the air/fuel mixture. Other surface processes concern material properties, corrosion, friction and wear.

Some years ago a project directed towards surface phenomena in combustion was established jointly by Volvo AB and the Physics Department of Chalmers University of Technology. The three subprojects that are currently being carried out concern: (i) exothermic catalytic reactions at atmospheric pressures, (ii) oxidation and catalytic properties of soot particles, and (iii) high temperature reactions on ceramics. This paper describes the equipment constructed for these studies and results from the first two subprojects.

2. Experimental system and procedure

A schematic overview of the experimental system is shown in fig. 1a. It consists of a turbopumped all metal UHV system (base pressure $\sim 1 \times 10^{-9}$ Torr) with provisions for XYZ sample manipulation, resistive heating and LN₂



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reaction cell and sample exchange lock. The cell is opened/closed via rotary motion of the screw (K), which moves the tube (J) and the flanges (H) and evaporation, flash desorption). For studies of reactions at higher pressures, the sample is moved into the reaction cell (see (b)). (b) The combined (N) up/down. The cell volume is sealed off from the main chamber by an O ring. The sample can be heated or cooled via the leads (T) and a pair of current/coolant feedthroughs. Continuous gas sampling to the mass spectrometer even at atomospheric pressure is obtained by the quartz tube leak (a) Fig. 1. (a) The experimental setup. The sample can be moved on a circle to the different analysis or preparation positions (AES analysis, ion sputtering, feeding gas to the mass spectrometer via the valve V3. cooling down to -150° C, and sample preparation by ion sputtering and evaporation. Auger Electron Spectroscopy is used for surface composition control (and for kinetic studies), and mass spectrometry is used for detection of gaseous reaction products and control of reactant gas mixtures. One of the most important parts of the experimental system is the reaction cell shown in detail in fig. 1b. Combined with a special construction [2] of the sample holder, this reaction cell allows quick transfer of the sample between the main UHV chamber and atmospheric pressure reaction conditions to be made. When the sample is enclosed in the reaction cell it can still be heated and cooled since it is still attached to the heating/cooling feedthrounds on the sample manipulator flange. With atmospheric pressure in the reaction cell the leak rate into the main chamber is less than 10^{-8} Torr $\cdot 1/s$. When a reaction sequence is run in the reaction cell, continuous control of the gaseous reaction products is obtained via a gas sampling device [3] feeding gas from a point < 1 mm away from the sample surface to the ion source of the masspectrometer.

The reaction cell also serves as a sample exchange lock, allowing sample changes to be made without breaking the vacuum of the main chamber. Access to the sample is obtained by removing the top flange of the reaction cell. Details of the construction and of the performance of the reaction cell are presented elsewhere [2], and its construction and performance are compared to other recently published [4–7] technical solutions of the same problem.

The two types of samples used in the studies reported here were Pt wire and evaporated carbon respectively. The Pt wire was of 0.125 mm diameter and 18 mm length, and with 99.995% nominal purity (Materials for Research, Marz grade). The sample was mounted in a four-point probe arrangement (see ref. [8]) and spotwelded to the sample holder. Before mounting, the sample was subjected to conventional washing procedures for UHV parts, but no additional chemical cleaning was undertaken. The final cleaning or "activation" was performed in a hydrogen-oxygen mixture in the reaction cell as described in section 3 (see also ref. [8]).

The carbon samples were evaporated from spectroscopically pure carbon rods by electron bombardment of the tip of the pencil-shaped carbon rod. Considerable efforts were required before the electron bombardment source produced pure C films as judged from the AES spectra [9]. The C films were deposited on well outgassed Au foils, to a final thickness of about 20 Å. The growth and subsequent removal by oxidation of the C layer was followed by recording the AES signals for gold and carbon. AES spectra were recorded by a 10 keV Varian cylindrical mirror analyzer. Further details on the experimental proceudre are given in ref. [9].

3.1. Correlation between catalytic activity of Pt and surface concentratios of O and Si

In a previous investigation [8] we observed that Pt samples of the kind used here showed a very low activity for the $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ reaction in a 4% H_2 + air mixture at temperatures below 150°C. At these temperatures the reaction rate accelerated in an uncontrollable manner due to self-heating, until the reaction became mass transport controlled. This transition from a low-rate kinetically-controlled reaction to a high-rate mass-transfer controlled reaction is a well-known phenomena in catalysis, called ignition. We found that the ignition temperature could be lowered by running the reaction at temperatures > 500°C in a high flow of the reaction mixture. After this activation an ignition temperature of around 50-60°C was observed. If the catalyst was run in the reaction mixture or several ignitions were performed in sequence, the ignition temperature continuously increased to the very reproducible value around 150°C. It was quite obvious to suspect that some chemical change of



Fig. 2. Ignition temperature as a function of the number of ignitions for the H₂ oxidation on Pt. Each point in this diagram is obtained from a run like that shown in the inset, which displays mass spectrometer signals and Pt wire temperature as a function of time as the Pt wire was slowly heated resistively. Note the rapid increase in the reaction rate at $130^{\circ}C = T_{ign}$. The rapid temperature rise is due to the increased chemical power dissipation.

the surface was responsible for the behaviour, but it remained a guess since no surface sensitive spectroscopic method was available at that time.

We have now repeated these measurements in the equipment described here. Fig. 2 shows the increase in ignition temperature with each new ignition. Directly after activation (10 min at 600°C in 3.5% H_2 in air) the ignition temperature is 60°C, and then monotonically increases to the asymptotic value of about 150°C.

Each data point was obtained from a temperature curve like the one shown in the inset in fig. 2, where the H_2 , O_2 and H_2O mass spectrometer signals, and the temperature are given as a function of reaction time. The reaction mixture (3.5% H_2 in air) was flowing continuously through the reaction cell, while the Pt filament was raised in temperature by stepwise increasing the heating current. By the four-point probe arrangement the resistivity and thus the temperature of the filament was obtained. When the filament reached the ignition temperature, the temperature increased rapidly due to self-acceleration until the mass-transport-controlled steady state was established. The reaction sequence was then interrupted by switching off the heating current and removal of the reaction gas mixture. The reaction cell was then evacuated and the sample moved to the AES position for spectroscopic investigation of the surface.

By inspection of AES spectra taken at different ignition temperatures, we have unambiguously shown that the increase in ignition temperature intimately correlates with increases in both the oxygen and the silicon content of the surface. Fig. 3, which shows AES spectra taken at different ignition temperatures, illustrates this point. The spectra were recorded with 8 keV primary electron energy. Using data from The Handbook of Auger Electron Spectroscopy (Physical Electronics Industries) we estimated the silicon and oxygen concentrations in curve d to be ≤ 0.5 monolayers. The energies of the Pt, Si and O peaks were 58, 74, and 501 eV, respectively.

We have also found that activation of the catalyst in the reaction mixture at temperatures > 600°C is superior to heating in pure H_2 or in vacuum. For example the ignition temperature is lowered from 150 to 60°C (and the Si and O signals reduced accordingly) by 10 min heating at 600°C in the reaction mixture. Heating in vacuum at 800°C also reduced the ignition temperature and Si and O signals, but after 10 h of heating the ignition temperature was still 76°C.

In our short discussion of these results we first note that the appearance of relatively large concentrations of Si on surfaces of high purity Pt samples has been reported recently in the literature [10,11], and attributed to segregation of impurity bulk Si. Bonzel et al. [10] studied this in some detail and determined the equilibrium surface concentration of Si as a function of surface temperature. The possible role of Si in the "strong" chemisorption of oxygen or surface oxide formation on Pt has also been discussed [10,11]. The energy of the Si auger peak is close to that observed in oxidized silicon, which might suggest a



Fig. 3. AES spectra recorded from the Pt wire sample. Each spectrum corresponds to a different ignition temperature for the H₂ oxidation reaction: (a) ~ 70°C, (b) 112°C, (c) 129°C and (d) 140°C.

chemical interaction between O and Si on the Pt surface. Niehus et al. have summarized the properties of the so-called strongly bound oxide [11], and we find that the properties of the oxygen on our Pt samples agree with their criteria concerning temperature stability and resistance towards heating. However, "our" oxide is formed under quite different conditions, namely during the catalytic reaction between H_2 and O_2 , and at lower temperatures.

The nature of strongly bound oxygen and its influence on catalytic properties of Pt have also been discussed in several papers [12–14]. However, to our knowledge there has been no study unambiguously correlating the presence of these impurities with catalytic activity for the H₂ oxidation reaction. Smith et al. [13] observed an *increase* in the catalytic activity of the oxidized surface for the dehydrogenation and hydrogenation reactions, and McCabe and Schmidt [14] observed new states for CO and H₂ with higher binding energies than on clean Pt. Contrary to this we find that the surface Si and O dramatically decrease the activity for the H₂ + O₂ reaction. Our data demonstrate a direct connection between the decrease in catalytic activity for the H₂ oxidation reaction and the increase in the Si and O concentrations. It still remains an open question whether Si or O, or both, are responsible for the catalytic activity decrease, or whether Si is only indirectly responsible by catalyzing the Pt surface oxidation. Work is in progress in our laboratory to answer these questions.

The observation that activation in an H_2/O_2 mixture is much more efficient than heating in vacuum or in a reducing H_2 atmosphere suggests that the processes taking place during the catalytic reaction between hydrogen and oxygen (e.g. the presence of OH) promote the removal of Si and O.

3.2. Oxidation of thin carbon layers

Some of the important questions about soot particles that relate to surface physics are: (i) What are the adsorption properties of soot particles? (ii) What are their catalytic properties for various chemical reactions? (iii) How do foreign elements in the particles modify their reactivity (particularly their oxidation properties) and catalytic properties? (iv) Can representative soot particles by synthesized in a controlled way from pure carbon?

In our research on the subject we decided to start from very thin layers of pure carbon to obtain a reference frame for studies of the much more complicated soot particles.

We report here on the oxidation rates measured for impurity-free (as judged by AES) evaporated carbon layers ≤ 20 Å thick, deposited on Au foils. Oxidation was performed at $P_{O_2} = 5 \times 10^{-4}$ Torr at five different temperatures: 450, 500, 550, 590 and 700°C. The oxidation rate was obtained by dividing the oxidation into short periods interrupted by AES measurements of the C and Au signals.

As the carbon film oxidized to CO and CO_2 , it became thinner and the C signal eventually diminished to zero while the Au signal grew from a low value to the value for the clean Au substrate.

Fig. 4 shows the Au and C signals as a function of oxidation time for different sample temperatures. From such curves we have calculated the oxidation rates assuming the C layer to be of uniform thickness and using simple electron escape depth theory. Calibration was obtained by building up a thick C layer, making a large number of identical C evaporations (~ 0.5 Å each) and recording an AES spectrum for Au (69 eV) and C (272 eV) between each evaporation. The Au and C signals were found to be well described by $\exp(-d/d_{Au}\cos\varphi)$ and $1 - \exp(-d/d_{C}\cos\varphi)$,

respectively. Here, d is the C layer thickness and φ the analyzer acceptance angle. For the electron escape depths we used literature values of $d_{Au} = 4.5$ Å [15] and $d_C = 7.5$ Å [15,16]. These data were then used to calculate the removal rate of C by oxidation in O₂ gas. The derived absolute oxidation rate at 700°C



Fig. 4. AES signals for C and Au as a function of oxidation time. The initial sample was a ~ 20 Å thick C film evaporated on a Au foil. With incressed oxidation time, the C film thickness was reduced by oxidation to CO and CO₂.

is about 8×10^{-3} Å/s, corresponding to a reaction probability of 4×10^{-5} per oxygen molecule striking the surface. The corresponding values at 500°C are 4×10^{-3} Å/s and 2×10^{-5} . The 700°C value agrees well with the reaction probability at 700°C that we extrapolate from the higher temperature data of Olander et al. (ref. [17], fig. 3). Their experiment was performed on an unannealed (defect-rich) sample of pyrolytic graphite (basal plane) with an oxygen molecular beam. Annealed samples showed much lower reaction probabilities.

The reaction products of the C film oxidation are mainly CO and CO_2 , but some oxygen was also found to be strongly bound in the C film [9]. No quantitative measurements of the relative CO/CO_2 ratio have as yet been performed.

4. Summary

We hope to have demonstrated that the established methods of surface phsyics can give new and valuable information on some processes in combustion. The combination of surface analytical tools, UHV preparation procedures, and gas analysis instrumentation with an integral reaction cell where reactions can be performed at real pressures gives a good platform for studies of, e.g., catalytic effects, soot particles and some materials science related problems in combustion research.

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