

Sensitivity Analysis of the Reaction Mechanism for Gas-Phase Chemistry of $\text{H}_2 + \text{O}_2$ Mixtures Induced by a Hot Pt Surface

M. FÖRSTH*

Department of Experimental Physics, Chalmers University of Technology and Göteborg University, SE-41296 Göteborg, Sweden

Sensitivity analysis has been used to study the gas-phase chemistry near a hot catalytic wall. The gas mixture was H_2/O_2 in different proportions and the studied pressure range was 1 to 10^5 Pa. The reaction mechanism for a polycrystalline Pt surface was used to model the catalyst surface, at a temperature of 1300 K. It is found that the chemistry of water production is relatively simple. For pressures of 1 to 10^3 Pa it is the transport of reactants to the surface, via sticking, which determines the water concentration in the gas-phase. For these low pressures almost all water is produced on the surface since there is no combustion zone in the gas. The water which is produced on the surface will desorb and then escape from the reactor without any further reactions. The situation is much more complex when an intermediate species, such as the O atom, is considered. O atoms in the gas-phase are prone to react with other species. This gives a complicated interaction between the surface and the gas-phase chemistry. The consumption of O atoms in the reaction $\text{O} + \text{H}_2 \rightleftharpoons \text{OH} + \text{H}$ is a major inhibitor for the O-atom concentration. It is found that the O atoms which are created in the gas originate mainly from desorbed OH, since the reaction $\text{H}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{H}$ yields H atoms which contribute to O-atom production in the reaction $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$. For the higher pressure range 10^4 to 10^5 Pa, there is a flame front at a certain distance from the surface, and the surface reactions are far less important than the gas-phase reactions. The reactions differ considerably in importance depending on whether the gas is fresh or burnt. © 2002 by The Combustion Institute

INTRODUCTION

The present paper reports numerical steady-state studies of the influence of a catalytic Pt surface on the gas-phase chemistry for the $1/2\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$ reaction in a stagnation-point flow reactor. This simple combustion process has the advantage of not involving carbon, which decreases the number of intermediate reactions considerably and thereby facilitates the analysis. The importance of gas-phase effects in heterogenous catalysis cannot be over-emphasized because the pressures in many industrial applications are much higher than those in laboratory experiments.

Catalytic Combustion

In most studies of catalytic combustion the focus is on the surface chemistry and on the transport of reactants to the surface; see for example [1–9]. However, in some cases the gas-phase does not only act as a reservoir for reactants but also participates in the overall

chemistry. An example of this is the catalytically stabilized thermal (CST) combustor [10], where a catalytic surface induces gas-phase combustion in a plug-flow reactor. Reference [10] also contains a good review of catalytic combustion in general, up to 1986.

Stagnation-Point Flow Calculations

Simulation of combustion processes is typically carried out in one of two ways. First, the complex geometry of, for example, a gas turbine or an internal combustion engine is fully retained, the geometrical details being described with a mesh. This is the approach in computational fluid dynamics, CFD, where on the other hand the chemistry may be very simplified if the computational expense must be kept reasonable. The second way, used in this paper, is to find suitable simplified model geometry but keep the full chemistry resolved into elementary reactions.

For studies of heterogeneous systems there are two geometries which are particularly useful [11]. One is the flat-plate boundary layer geometry [1], where the gas flow is parallel to the

*Corresponding author. E-mail: forsth@fy.chalmers.se

surface. The other is the stagnation-point flow geometry, used in this paper. In this geometry the gas mixture flows perpendicularly toward the surface, and the computations are simplified by a similarity transformation of the flow field [12, 13].

One of the earliest observers of the catalytic effect on flammable gas mixtures was Sir Humphrey Davy in the middle of the 19th century [14]. In another relatively early study [15] the effect of hot platinum and nickel bars on mixtures of natural gas and air was investigated. In a later study [16] a relation for the ignition conditions of flowing gases at hot bodies [17] was extended to conditions of non-steady state, for example the ignition delay from sudden heating to gas-phase ignition. This type of process occurs, for example, in ignition by electrical sparks in Otto internal combustion engines.

An analysis of the transient ignition of a combustible mixture by a hot, isothermal body with a non-catalytic surface inserted in a stagnant flow was made in [18] and [19]. Both catalytic and gas-phase ignition, as well as extinction, were studied at atmospheric pressure in [20]. A critical examination of the experimental and theoretical work until 1982 concerned with methane/air ignition by hot surfaces is given in [21].

An early study with planar laser-induced fluorescence of the OH molecule, OH PLIF, and a 2-D array detector was made in [22–24]. The process of gas-phase ignition in an atmospheric-pressure ethane/air flat plate boundary layer geometry, over heated catalytic and non-catalytic surfaces, was investigated. The experimental setup was meant to simulate the entrance of a catalytically stabilized thermal (CST) combustor [10].

A computational study of methane/air combustion over heated catalytic and non-catalytic surfaces was made in [25]. The effect of different surface-reaction boundary conditions on flame propagation and on the development of radical profiles in the gas-phase was studied. The effects of desorption of OH radicals from the surface on the radical profiles and on the flame propagation was also studied. It was shown that an accurately measured temperature profile as temperature boundary condition was necessary to decouple temperature effects and

species boundary condition effects on the development of radical profiles.

In [26] reduced gas- and surface-chemistry models were developed for surface and gas ignition of H₂/air mixtures over platinum in stagnation-point flow geometry. Simplified transport models were also studied. The authors point out that caution is needed in applying reduced mechanisms developed for homogeneous combustion to catalytic combustion.

In [27] operational windows for successfully and safely running a real catalytic combustor have been identified. Also, control strategies to arrive at these windows were discussed.

Because the literature on surface effects on homogeneous combustion is very rich, the papers reported above constitute a very brief overview. The complex literature on surface chemistry on Pt-surfaces is discussed in section “Surface-Phase Reaction Kinetics,” in the Theory chapter below.

Sensitivity Analysis

Sensitivity analysis is often used as a tool to obtain reduced reaction mechanisms. Examples of this can be found in, for example, [28], where the reaction mechanism for oxidative coupling of methane is reduced from 164 to 31 reactions, or [29], where the number of reactions for methanol/oxygen gas-phase thermolysis is reduced from 48 to 31. A severe test on a reduced mechanism is if it can reproduce oscillations in time. Such a reduction scheme was worked out in [30], where the mechanism for the oscillatory oxidation of hydrogen in a continuously stirred tank reactor, CSTR, was studied and reduced. There are two main reasons to work out reduced reaction schemes. The first is that in a reduced reaction scheme the most important reactions and species are extracted, so one can more easily obtain a fundamental understanding of the overall process. The second reason is that reduced reaction schemes, with a minimum of species and reactions in the model, require less computing time, which is important in complex CFD calculations, as mentioned above.

In [31] the sensitivity of the ignition temperature of H₂/air mixtures to surface reaction pre-exponentials, to gas-phase species diffusion coefficients, and to energy conduction was stud-

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