

Catalytic Ignition and Extinction of Very Fuel-Lean Hydrogen-Air Mixtures on Platinum Surfaces

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Abstract: Surface ignition and extinction of very fuel-lean hydrogen-air mixtures on platinum surfaces were modeled using a detailed surface kinetic mechanism and transport phenomena. A stagnation-point flow geometry was employed to study the effect of heat flux, flow velocity, and composition on the surface ignition and extinction. The temperature and concentration on platinum surfaces as well as the coverage of surface species were also explored to evaluate the role of gas-phase chemistry. It was shown that the platinum surface can be poisoned by different adsorbates, and the dynamic process of surface ignition and extinction is associated with a phase transition from one poisoning species to another. For certain temperatures, multiple poisoned states of the surface coexist. Comparisons of simulations with experiments were carried out, and the results revealed that the self-inhibition of hydrogen surface ignition is caused by poisoning of platinum by atomic hydrogen.

Keywords: Surface Reaction, Surface Kinetics, Adsorption Kinetics, Desorption Kinetics, Platinum Surface, Catalytic Ignition

1. Introduction

Ignitions, extinctions and multiplicities in surface reactions are important in many applications, including partial oxidation reactors for chemical synthesis and catalytic removal of pollutants. These instabilities delimit the regime of operation of many industrial catalytic reactors and play a major role in reactor safety. Some pathological trends of ignition and extinction have been observed on platinum surfaces. In particular, the self-ignition temperature of carbon monoxide in air rises with feed composition [1], whereas the extinction temperature drops with feed composition. This behavior cannot be explained using a one-step surface reaction with either a positive or a negative order in fuel kinetics. The increase of self-ignition temperature with feed composition, i.e., self-inhibition behavior, has also been observed for hydrogen and olefins but not for paraffins [2]. However, a clear understanding of the reaction mechanism causing this self-inhibition behavior for some fuels has not been yet achieved.

Previous studies on prototype reaction systems with simple surface chemistry have shown that competition between

adsorbates for catalyst sites can result in rate multiplicities and fluctuations [3]. These multiplicities can occur under isothermal conditions where the exothermicity of surface reactions is not a prerequisite as a feedback mechanism. Despite the fact that there are numerous studies on surface multiplicities and phase transitions [4], there are no studies on surface multiplicities of oxidation reactors using detailed surface kinetics. Therefore, how previous results can be generalized for detailed surface reaction mechanisms is still not clear. On the other hand, the advance in surface chemistry for simple adsorbates on some catalysts allows detailed modeling of these systems.

In this study, surface ignition and extinction of very fuel-lean hydrogen-air mixtures on platinum surfaces were investigated, using a stagnation point-flow model with detailed surface kinetics and transport phenomena. A stagnation-point flow geometry was considered because it is a widely used experimental configuration and makes mathematical analysis tractable. Additionally, it represents a well-defined flow field with a zero-dimensional catalytic surface, which enables coupled modeling of heterogeneous chemistry and reactive flow at steady-state and transient conditions. The flow is towered to a disk by creating a

stagnation point on the disk to achieve a thick and uniform deposition across the substrate.

2. Computational Methods

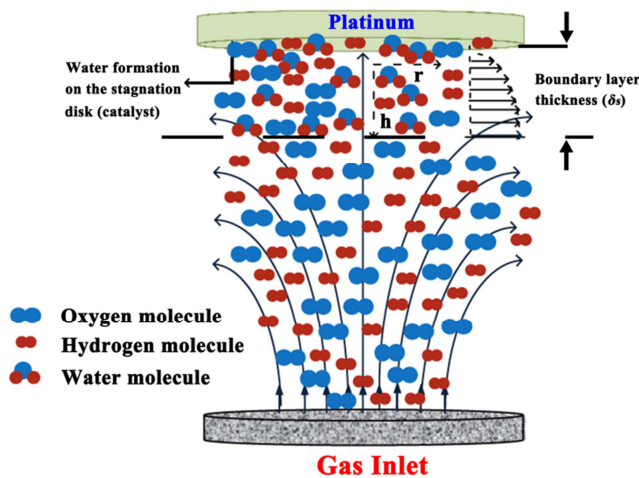


Figure 1. Schematic diagram of the simulated stagnation flow reactor.

A stagnation-point flow geometry is modelled, as shown schematically in Figure 1. Premixed hydrogen-air mixtures impinge on a flat platinum surface. The ideal-gas law is employed as an equation of state. The conservation equations of continuity, momentum, energy, and species for axisymmetric flow are employed. The surface chemistry on the platinum surface is modeled through appropriate mass-transfer boundary conditions. The feed composition is fixed. The composition above the surface, which determines the state in the continuum flow regime, is an unknown of the problem in the continuum flow regime, given that the mean free path is relatively low, compared to the characteristic dimensions of the reactor. The unknown surface composition is determined from the surface boundary condition of species. Concerning the species boundary conditions, the flux of a gas-phase species at the surface is equal to its net rate of consumption because of interfacial reactions. Interfacial reactions are defined as these reactions which include at least one surface species. For a surface species, at steady state the net reaction rate is equal to zero. Finally, the coverage of vacancies is computed from an overall balance on catalyst sites.

Simulations are performed at ambient temperature and atmospheric pressure. A second order finite difference scheme is used to discretize the differential equations. The arc-length continuation techniques and Newton-Raphson method are employed to solve the coupled algebraic equations. A typical simulation involves approximately 10^3 equations and approximately 10^3 unknowns and requires several hours, when parallel processing is used for a one-parameter continuation run.

The surface reaction mechanism of Deutschmann *et al.* [5] is used. The surface mechanism used is of the Langmuir-Hinshelwood type. The stable product in the catalytic oxidation of hydrogen is water. Hydrogen and

oxygen dissociate upon adsorption to H^* and O^* , respectively (* denotes adsorbed species). H^* and O^* desorb by bimolecular association to form hydrogen and oxygen, respectively. H^* reacts with O^* to form OH^* . Since the desorption of OH^* is highly activated, OH^* is preferentially converted to H_2O^* . H_2O^* desorbs readily at relatively low temperatures to form water in the gas phase. Second-order adsorption and desorption kinetics for hydrogen and oxygen are used here. Interfacial reactions include the competitive dissociative adsorption of hydrogen and oxygen, the competitive adsorption of water, the re-combinative desorption of H^* and O^* into hydrogen and oxygen, respectively, the desorption of H_2O^* and OH^* , and surface reactions [6]. This mechanism has been tested against experimental ignition data, and good agreement has been found [7]. The gas-phase reaction mechanism of Burke *et al.* [8] is employed, which has been tested against a wide range of combustion targets.

3. Results and Discussion

3.1. Surface Temperature and Concentration

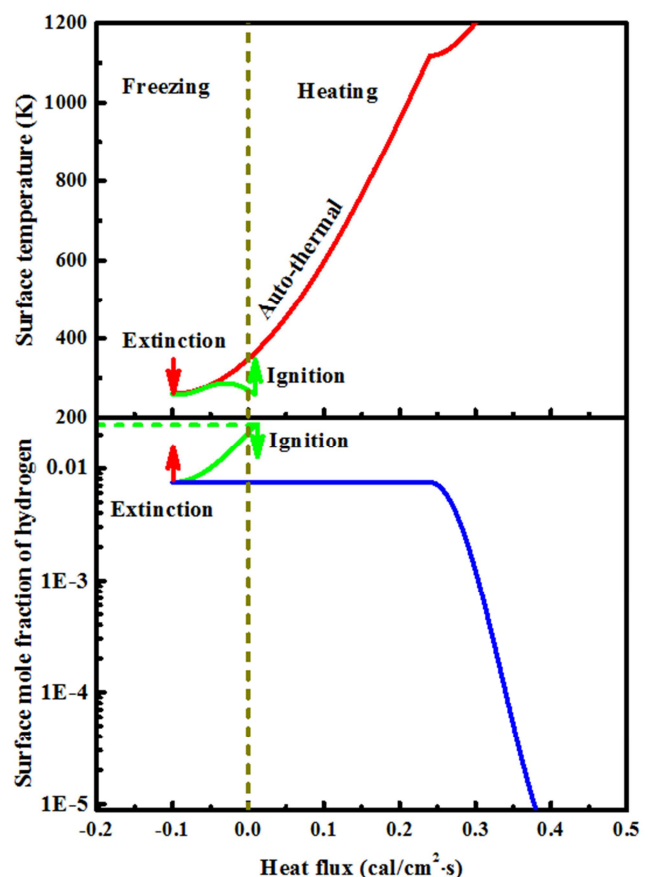


Figure 2. Effect of heat flux on the surface temperature and the mole fraction of hydrogen at the gas-surface interface. A mixture of 0.8% hydrogen in air with a strain rate of 50 s^{-1} is considered.

Figure 2 shows the surface temperature and the mole fraction of hydrogen at the gas-surface interface as a function of heat flux. The heat flux is provided to the

surface by resistive heating of the platinum foil for 0.8% hydrogen in air [9]. Neither radiation nor heat losses at the back of the platinum foil are considered here because the ignition temperatures are low. At zero power, the surface temperature is equal to ambient temperature. As the power increases, the surface temperature increases almost linearly, and the reactivity of hydrogen is negligible. At a certain critical value of power, a turning point is found, which is indicated with a vertical arrow, where the system ignites. The corresponding temperature is called an ignition temperature.

Upon ignition, the system jumps to the ignited branch. An increase in surface temperature and a decrease in the hydrogen mole fraction will then be observed. In simulations, an intermediate unstable branch connects the ignited and extinguished branches. For reasons of clarity and because of the multiple curves, all branches are drawn using the same marking. As the power increases on the ignited branch, at approximately 1100 K a change in the slope of the surface temperature-heat flux curve can be observed. At this point, the surface mole fraction of hydrogen decreases sharply with the power input to the surface, indicating the onset of gas-phase chemistry.

As the power decreases from high values along the ignited branch, a critical point is reached where surface reactions cannot be further self-sustained. This point corresponds to an extinction indicated by a vertical arrow. The extinction temperature is below ambient temperature for these operating conditions, i.e. freezing of the surface is needed to extinguish surface reactions. The temperature on the ignited branch where surface reactions can be self-sustained, i.e. at zero power, is called an auto-thermal point. This point divides the space into the freezing and heating subspaces.

3.2. Role of Gas-Phase Chemistry

Until recently, gas-phase chemistry has been generally ignored in simulations, even though experiments have provided evidence towards the presence of vigorous gas-phase reactivity under certain operating conditions [10]. To examine the role of gas-phase chemistry in the catalytic oxidation of hydrogen, simulations are performed while suppressing gas-phase reactions. Figure 3 shows the effect of gas-phase chemistry on the surface temperature and the mole fraction of hydrogen at the gas-surface interface. Gas-phase chemistry has essentially no effect on the catalytic ignition and extinction temperatures. However, deviations between the two simulations, with and without the gas-phase chemistry, can be observed when the surface temperature is above approximately 1100 K. When the mole fraction of hydrogen is plotted versus temperature instead of power, the change in slopes corresponds to an actual turning point, i.e., ignition [11]. This is similar to the homogeneous ignition found in earlier work of Bui *et al.* [12]. Therefore, this change in slope at approximately 1100 K indicates the onset of homogeneous reactions.

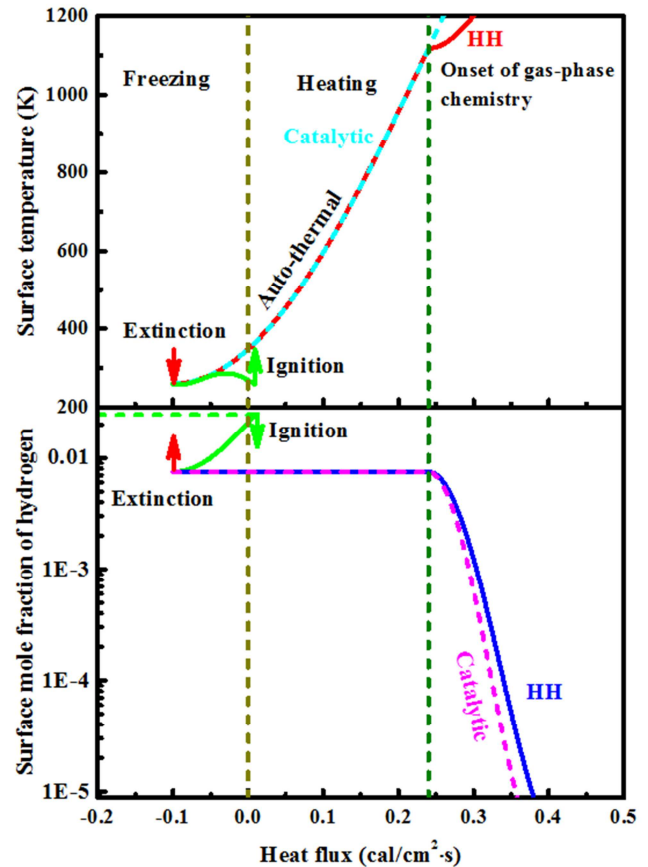


Figure 3. Effect of gas-phase chemistry on the surface temperature and the mole fraction of hydrogen at the gas-surface interface. The solid lines indicate the coupled homogeneous-heterogeneous (HH) process with gas-phase and surface chemistry, and the dashed lines correspond to the catalytic process alone without gas-phase chemistry.

3.3. Surface Coverage

Figure 4 shows the coverage of surface species as a function of the power input to the surface. For temperatures below the catalytic ignition temperature, the surface is covered with atomic hydrogen H^* . Thermodynamically, atomic oxygen is preferred at low temperatures on platinum surfaces compared to atomic hydrogen because of the high heat of adsorption of oxygen [13]. However, the entire system is not in thermodynamic equilibrium [14]. The high rate of adsorption of hydrogen, because of its low molecular mass and its higher sticking coefficient compared to oxygen [15], leads to preferential dissociation of hydrogen. Since the activation energy for desorption of H^* is relatively high and the temperatures are low, the fraction of free platinum sites (vacancies) is very low, and oxygen cannot dissociate (an " H^* -poisoned" surface). As a result, the surface reaction rates and the conversion of the fuel are low. A similar behavior has been observed in the catalytic oxidation of carbon monoxide [16].

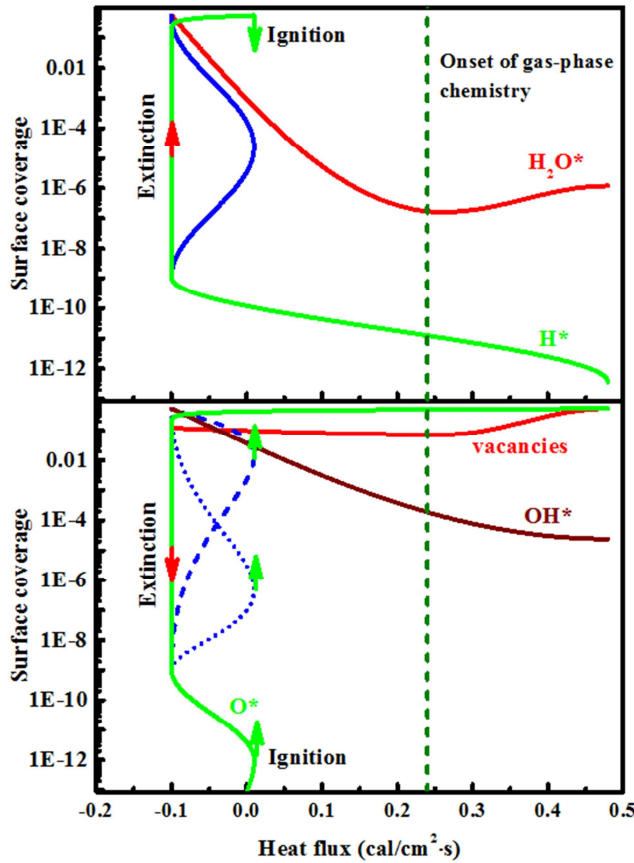


Figure 4. Effect of heat flux on the surface coverage of species for the coupled homogeneous-heterogeneous process. Upon ignition, a transition from an H^* -covered surface to an O^* -covered surface occurs. Upon extinction, a transition from an H_2O^* -covered surface to an H^* -covered surface occurs.

Upon ignition, the platinum surface becomes covered with atomic oxygen O^* , i.e. during the transient process of catalytic ignition, a phase transition from an H^* -covered surface to an O^* -covered surface occurs. This transition occurs because during ignition the small fraction of hydrogen becomes almost completely oxidized. Oxygen is then in such an excess above the platinum surface that its rate of adsorption is higher than that of hydrogen. Therefore, oxygen dissociates to O^* . This transition from an H^* -covered surface to an O^* -covered surface is because of a change in partial pressures of reactants above the surface, as determined by the surface boundary condition. Since the desorption of O^* is highly activated, at temperatures below the homogeneous ignition temperature, the surface is partially poisoned by O^* . A small fraction of vacancies at intermediate temperatures allows for a small reactivity on this branch.

On the ignited branch, as the power decreases, OH^* and H_2O^* increase at the expense of O^* . Near extinction, i.e., low temperatures, H_2O^* cannot desorb and blocks most catalyst sites, i.e., a product poisoning. During extinction, the platinum surface converts from $(H_2O^* + OH^*)$ -blocked to H^* -blocked.

The simulations reveal that the multiple poisoned phases can coexist at the same temperature. Outside the multiplicity regime, the surface is covered by one of the adsorbents (H^* or O^*), and within the multiplicity regime, the surface can be

covered by one of the adsorbents, the product (H_2O^*), and an intermediate (OH^*).

3.4. Effect of Flow Velocity

The above simulations are performed for 0.8% hydrogen in air. In this section, the effect of flow velocity on the catalytic ignition temperature is examined, and the results are compared with experiments. At similar compositions, the catalytic ignition temperature is higher than experimental data. Sensitivity analysis reveals that the catalytic ignition temperature is affected mainly by the activation energy for desorption of H^* , and the sticking coefficients of hydrogen and oxygen (data not shown). As an example of illustrating the role of desorption of H^* , simulations are performed for different activation energies.

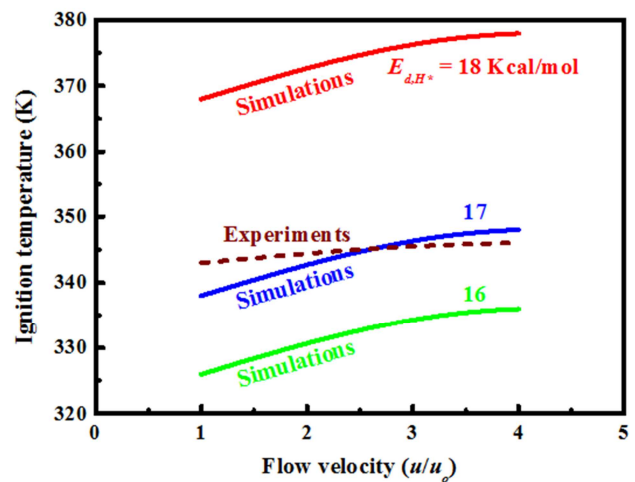


Figure 5. Effect of flow velocity on the catalytic ignition temperature. A mixture of 0.8% hydrogen in air for three values of activation energy of desorption of H^* is considered. The experimental results are obtained on platinum wires by restricting the flow to the low Reynolds number range. The scaling strain rate in the simulations is 50 s^{-1} , and the scaling velocity in the experiments is 5 cm s^{-1} .

Figure 5 shows the effect of flow velocity on the catalytic ignition temperature. The results are obtained from simulations using detailed chemistry by varying the strain rate, i.e., a velocity gradient outside the boundary layer [17]. For a nozzle at a fixed distance from the platinum surface, the flow velocity in simulations is proportional to the strain rate. The experimental results are obtained on platinum wires by restricting the flow to the low Reynolds number range, and the parameters studied include flow velocity, fuel type and concentration, and oxygen concentration [18].

Simulations show a slight increase in ignition temperature with the increase of flow velocity. However, both simulations and experiments indicate that the effect of transport phenomena on the catalytic ignition temperature is minor for these conditions, i.e. kinetics controls catalytic ignition. A different activation energy for desorption shifts the ignition curve but does not change the qualitative response of the system.

3.5. Effect of Composition

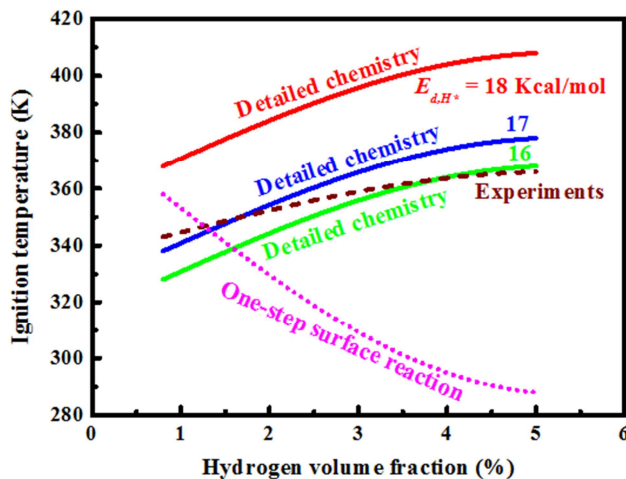


Figure 6. Effect of composition on the catalytic ignition temperature of hydrogen. The experimental results are obtained on platinum wires by restricting the flow to the low Reynolds number range.

In this section, the effect of composition on the catalytic ignition temperature is examined, and the results are compared with experiments. Figure 6 shows the effect of composition on the catalytic ignition temperature. Experimentally, the self-inhibition of hydrogen on its ignition temperature can be observed [19]. The experimentally observed trend of increasing ignition temperature with increasing hydrogen to oxygen ratio can be attributed to a combination of the hydrogen desorption kinetics and a weaker coverage dependence for hydrogen sticking than for oxygen sticking on the surface [20]. For example, The catalytic ignition temperature is determined by a competition between hydrogen site blocking on the surface and hydrogen desorption, which makes the catalytic ignition temperature increase with increasing hydrogen to oxygen ratio [21]. Additionally, the catalytic ignition of hydrogen is primarily governed by coupling between the heat balance, the kinetics of adsorption of hydrogen and oxygen, and the desorption kinetics of hydrogen [22]. Detailed chemistry predicts correctly this trend independently of the details of the reaction rate constants as far as the surface is blocked by H^* before ignition occurs.

Simulations have also been performed using a one-step surface chemistry. The rate of the global surface reaction is taken to be first order with respect to hydrogen and zero order with respect to oxygen, as suggested experimentally [23]. The pre-exponential and activation energy are adjusted so that ignition happens at a positive power [24], and the catalytic ignition temperature is close to experiments for 0.8% hydrogen in air [25]. The rate expression can be found in the previous work of Ikeda *et al.* [26], in which the interaction between heterogeneous and homogeneous reactions arising when a mixture of hydrogen and air impinges on a platinum plate at elevated temperature has been studied. The relevant kinetics parameters can be found in the previous work of Petersson and Ackelid [27] as well as Johansson *et al.* [28].

The one-step surface chemistry predicts the opposite trend from the experimental results. This promotion of ignition with composition is because of the fact that in the case of a global reaction, the catalytic ignition is caused by the exothermicity of the surface reaction. As the composition increases, more heat is released from the surface reactions, and thus the catalytic ignition occurs at lower temperatures. Qualitatively, the promotion of catalytic ignition with composition is insensitive to the details of the parameters of the one-step surface kinetics.

It has been found that the catalytic ignition of hydrogen is controlled by the slow desorption of H^* and the availability of free platinum sites. Therefore, the self-inhibition of hydrogen on its ignition is caused by an increase in the partial pressure of hydrogen above the surface with increasing composition, which results in a more effective blocking of platinum. A higher surface temperature is then needed for desorption of H^* to occur. Given the fact that the surface chemistry has been derived mainly at low pressures and is used here at atmospheric pressure, the qualitative agreement between experiments and simulations is very good. Here, the kinetics parameters do not adjust to fit the experimental data; rather, it is illustrated that self-inhibition is caused by blocking of the catalyst by the fuel or one of its fragments for more complex hydrocarbons. Improvements between simulations and experiments by including adsorbate-adsorbate interactions may also be possible.

4. Conclusions

The catalytic ignition of very fuel-lean hydrogen-air mixtures on platinum surfaces was studied, using a stagnation point-flow model with detailed surface kinetics. The main points can be summarized as follows. There is a small effect of transport on the catalytic ignition for the regime of flow velocities studied. The self-inhibition behavior found experimentally is also reproduced in simulations, and has been attributed to partial poisoning of the catalyst by atomic hydrogen at low temperatures. Catalytic ignition is controlled by desorption of atomic hydrogen. Upon ignition, the surface becomes poisoned by atomic oxygen until at higher temperatures homogeneous ignition takes place, i.e., the onset of gas-phase ignition. Near extinction, the surface is poisoned by the product water. These surface phase-transitions occur as the temperature and/or the partial pressures of reactants, i.e., composition, change because of a competition of adsorbates for catalyst sites. Coexistence of various poisoned states by intermediates and the product have been observed, using a mean-field model. The future work will focus on the role of surface reaction mechanisms, transport, and reaction exothermicity in the catalytic ignition of hydrogen and hydrocarbons.

Acknowledgement

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