Methane ignition catalyzed by in situ generated palladium nanoparticles

T. Shimizu\textsuperscript{a}, A.D. Abida, G. Poskrebshev\textsuperscript{a}, H. Wang\textsuperscript{a,}\textsuperscript{,}b, J. Nabity\textsuperscript{b}, J. Engel\textsuperscript{b}, J. Yu\textsuperscript{b,} D. Wickham\textsuperscript{c}, B. Van Deven\textsuperscript{d}, S.L. Anderson\textsuperscript{d}, S. Williams\textsuperscript{e}

\textsuperscript{a}Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA 90089, United States
\textsuperscript{b}Reaction Systems, LLC, 19039 E. Plaza Drive, Suite 290, Parker, CO 80134, United States
\textsuperscript{c}Department of Chemistry, University of Utah, Salt Lake City, UT 84112, United States
\textsuperscript{d}Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA 90089, United States
\textsuperscript{e}TDA Research, Inc., 12345 W. 52nd Ave, Wheat Ridge, CO 80033, United States

Abstract

Catalytic ignition of methane over the surfaces of freely-suspended and in situ generated palladium nanoparticles was investigated experimentally and numerically. The experiments were conducted in a laminar flow reactor. The palladium precursor was a compound (Pd(THD))\textsubscript{2}, THD: 2,2,6,6-tetramethyl-3,5-heptanedione) dissolved in toluene and injected into the flow reactor as a fine aerosol, along with a methane–oxygen–nitrogen mixture. For experimental conditions chosen in this study, non-catalytic, homogeneous ignition was observed at a furnace temperature of \sim 1123 K, whereas ignition of the same mixture with the precursor was found to be \sim 973 K. In situ production of Pd/PdO nanoparticles was confirmed by scanning mobility, transmission electron microscopy and X-ray photoelectron spectroscopy analyses of particles collected at the reactor exit. The catalyst particle size distribution was log-normal. Depending on the precursor loading, the median diameter ranged from 10 to 30 nm. The mechanism behind catalytic ignition was examined using a combined gas-phase and gas-surface reaction model. Simulation results match the experiments closely and suggest that palladium nanocatalyst significantly shortens the ignition delay times of methane–air mixtures over a wide range of conditions.

\copyright 2009 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Supersonic combustion has drawn attention in recent decades with possible applications to hypersonic propulsion systems. Hydrogen has long been used as a fuel for hypersonic systems due to its short ignition delay and fast kinetics. However, its low fuel density results in poor vehicle packaging. Conversely, liquid kerosene based jet fuels package well but have additional complications with regard to fuel injection and droplet vaporization leading to reduced combustion performance. Furthermore, liquid jet fuels tend to produce significant amounts of coke during endothermic cooling cycles. Thus, methane has gained interest for its potential to overcome most of these problems. It has greater heat sink capacity and specific energy content than jet fuels and a much higher energy density, if stored as a cryogenic liquid, than hydrogen [1]. However, the use of methane could lead to poor ignition performance. The current work explores the question whether ignition of methane can be enhanced catalytically by freely-suspended palladium (Pd) nanoparticles generated in situ from a suitable fuel-soluble Pd precursor. Entrained in the mixture, palladium particles are expected to provide catalytic surfaces to initiate gas-surface reactions, leading to fuel ignition at lower temperatures and/or with drastically reduced ignition delay times.

Catalytic oxidation of hydrogen and small hydrocarbons over palladium has been studied quite intensely in recent years [2]. It is known that the palladium exhibits complex hysteresis behavior with respect to the rate of methane oxidation over its surface and that the catalytic activity is influenced by the presence of water vapor [3] and can be sensitive to OH poisoning [4]. In general the catalytic reaction rate increases with an increase in temperature until about 900 K, above which the reaction rate decreases. Above 1050 K, the catalytic reaction rate increases again [3]. This complex behavior appears to be related to the variation of the bulk composition of palladium to be discussed below.

In an oxidizing environment, palladium oxide (PdO) is stable thermodynamically for temperatures of relevance to catalytic oxidation. The equilibrium constant \( K \) of

\[ 2PdO (s) = 2Pd (s) + O_2 (g) \]

has been reported to be \( 2.2 \times 10^{-3} \text{ atm} \) at 909 K and 0.64 atm at 1124 K [5]. Hence the preferred thermodynamic state is palladium oxide in air below \sim 900 K, but it dissociates into Pd(s) and O\(_2\)(g)
at temperatures above 1100 K. Kinetically, oxidation of the palladium surface can lead to penetration of oxygen atoms into the surface, creating local microstructures such as surface islands and peninsulas [6]. Studies of oxygen adsorption and desorption on palladium nanoparticles supported on FeOx show quite complex behaviors with respect to reversible chemisorption and surface oxide formation [7]. Hysteresis has also been observed for oxidation and reduction of Pd supported on Al2O3 [8]. Computationally it was shown that the hysteresis behavior is caused, at least in part, by the competition between adsorption and desorption of oxygen from the surface, coupled with the diffusion of oxygen into and from the atomic layers below the Pd surface [9]. In general, the studies discussed above were conducted at temperatures near or below 1000 K. Only a few studies have been reported for Pd catalytic kinetics above 1000 K. Notably, Rosen and coworkers [10,11] examined the reaction mechanism of hydrogen oxidation over a palladium surface in a stagnation flow reactor.

An added complexity is that the catalytic activity and mechanism on the surface of nanosized Pd particles can be different from a perfect Pd(1 1 1) surface [12]. These complexes indeed pose some significant challenges for initiating methane ignition with in situ generated Pd/PdO nanoparticles, especially when one considers the limitation of catalyst loading. The fundamental difficulty to achieve fuel ignition below 900 K is that the catalytic oxidation of the fuel must be designed in such a way that the reaction process transitions from a catalytic process with mild oxidation rates at low temperatures to a flame process driven by gas-phase free-radical chain branching above about 1400 K. Heat release from the catalytic process must occur, at least locally, to allow the gas to heat up and reach the cross-over temperature above which radical chain branching becomes possible. At the same time, the catalytic reaction and heat release cannot be too fast, since the flame, if ignited, must have sufficient fuel left to sustain and propagate itself.

Meanwhile, the Pd/PdO nanoparticles require a finite time to nucleate out of its precursor. This time must be shorter than the transit time through the combustor to allow the catalytic process to occur. On the other hand, if the nucleation time is too short compared to the transit time, particle–particle coagulation and coalescence would lead to a reduced surface area per unit mass of catalyst injected and a reduced catalytic activity. Additionally as the Pd/PdO particles grow in size and mass, they must pass through a cluster size regime where the catalytic mechanism is poorly understood.

Previously methane oxidation over a Pd surface has been studied in flow reactors [13,14]. In general, these studies used wall-coated Pd to accomplish low temperature oxidation (up to 1100 K) with the purpose of minimizing NOx formation. No studies have been reported on fuel ignition on Pd nanoparticles suspended in unburned fuel-oxidizer mixtures.

The objective of this study is to understand the catalytic ignition behavior of methane with Pd nanoparticles generated in situ. The study combines flow reactor experiments, aerosol and surface sciences with kinetic modeling using detailed gas-phase and gas-surface reaction kinetics to explore the underlying mechanisms of methane ignition over Pd nanoparticles. A combined gas-phase and gas-surface reaction model is proposed on the basis of previous studies [15,16]. Combined with microscopy, particle mobility sizing and other chemical analyses of the Pd particles, the model was used to explain the observations made in the flow reactor. This is not meant to be a quantitative kinetic modeling study. The use of a laminar flow reactor indeed limits our ability to account for local reaction conditions in a precise manner. Nonetheless the results described here are useful for designing a catalytic reaction process suited for high-speed combustion.

2. Experimental

Generation of palladium particles in situ and the subsequent ignition procedure is drawn in Fig. 1 schematically. The sequence of the nanoparticle formation process is described as follows. At the reactor inlet section, a Pd precursor solution diluted in toluene is introduced in the form of micron sized aerosol carried by nitrogen stream. This flow was mixed with a stream of premixed CH4/O2/N2 mixture. Due to the high temperature and small droplet size, the aerosol quickly evaporates in the inlet section of the reactor. Dissociation of the precursor follows due to heating, releasing Pd atoms or clusters. At high enough atom or cluster concentrations, Pd nucleates into small clusters which grow in size and mass by coagulation and surface condensation. The clusters or the surfaces of the nanoparticles become catalytically active at some point. The gas mixture is then expected to undergo catalytic oxidation and eventually ignite in the flow reactor. Here, we follow the concentrations of CH4 and CO2 to monitor fuel ignition.

2.1. Setup

A schematic flow diagram of the experimental setup is presented in Fig. 2. A flow tube reactor was built in conjunction with a detector for measurement of CH4 and CO2 concentrations at the exit of the reactor. The particles are also sampled at the reactor exit, enabling us to simultaneously measure the particle size distribution functions and catalytic activity during experiments.

The flow reactor is made of a quartz tube (1.9 cm OD, 1.7 cm ID, and 94 cm in length). Although by visual inspection the tubes were usually clean after each experiment, they were replaced after each experiment.

![Fig. 1. Conceptual drawing of in situ generation of nanoparticles followed by catalytic ignition of a fuel-oxidizer mixture in a flow reactor.](image-url)
experiment to minimize the influence of wall deposits. An insulated furnace (Mellen SV12) with the test section length \( L = 76 \, \text{cm} \) was used for heating. The furnace has two separate zones. The temperature in each zone was measured using a thermocouple (OMEGA K-type). The measured temperatures are denoted as \( T_{f-1} \) (TC-1, Zone I) and \( T_{f-2} \) (TC-2, Zone II), respectively. These temperature values were acquired by the LabVIEW™ program and used to control the furnace temperature. The temperature profiles inside the reactor were measured using 122 cm long K-type thermocouples (OMEGA) inserted from the reactor exit (TC-3).

The gas mixtures were prepared by mixing CH\(_4\), N\(_2\), and O\(_2\) from cylinders. The flow rates were controlled by mass flow controllers (Porter Model 201) calibrated for each of the gases. The mixture composition tested and the total gas velocity \( U_0 \) selected are summarized in Table 1. The residence time in the reactor was about 1 s at the temperature of reactor operation. The reactor exhaust was diluted eight times by a cold stream of N\(_2\). The flow rate was controlled by a mass flow controller (Porter Model 202). The concentrations of CH\(_4\) and CO\(_2\) at the exit of the reactor were continuously monitored using an NDIR gas analyzer (California Analytical Instruments Model 200), which withdraws 2 L/min of the diluted exhaust gas.

The precursor atomizer was designed to produce micron sized droplets suspended in a N\(_2\) flow. The atomizer utilized a dual, concentric nozzle design, as shown schematically in Fig. 2, whereby a compressed N\(_2\) flow passes through the inner nozzle (2 mm ID glass tubing with a tip diameter of 0.5 mm). Under this condition, the Venturi effect draws the precursor solution from a liquid pool through the outer nozzle (4 mm ID glass tubing with a tip diameter of 1 mm), forming a stream of aerosol.

The atomizer outlet used 6.53 mm ID tubing and an elbow to form a series of impactors, thus eliminating the passage of large droplets into the reactor. The large droplets collected onto the impactors were returned to the liquid pool. The aerosol production rate depends on the liquid pool level, the flow rate of N\(_2\), and the position of the impactors. The N\(_2\) flow rate through the atomizer was controlled manually with a needle valve and an upstream pressure indicator (PI-1). The liquid pool was replenished with a single piston syringe pump (Chrom Tech ISO-1000), resulting in steady operation of the atomizer. The atomizer was cooled and insulated to avoid evaporation of the droplets collected on the inner wall, which would precipitate and crystallize the precursor onto the wall.

Pd(THD\(_2\)) \( (\text{THD}: 2,2,6,6\text{-tetramethyl-3,5-heptanedione}) \) (molecular weight 475 g/mol, sublimation temperature 150 \( ^\circ\)C at

\[ \text{Table 1} \]

<table>
<thead>
<tr>
<th>No.</th>
<th>Total gas velocity (STP), ( U_0 ) (cm/s)</th>
<th>Mole fraction</th>
<th>Equivalence ratio, ( \phi )</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(_2)H(_8)</td>
<td>CH(_4)</td>
<td>O(_2)</td>
<td>N(_2)</td>
</tr>
<tr>
<td>F-0</td>
<td>52.9</td>
<td>–</td>
<td>–</td>
<td>1.000</td>
</tr>
<tr>
<td>F-1</td>
<td>52.9</td>
<td>0.007</td>
<td>0.084</td>
<td>0.420</td>
</tr>
<tr>
<td>F-2</td>
<td>52.5</td>
<td>0.007</td>
<td>0.084</td>
<td>0.420</td>
</tr>
<tr>
<td>F-3</td>
<td>52.5</td>
<td>0.007</td>
<td>–</td>
<td>0.420</td>
</tr>
</tbody>
</table>

\( \phi \) Calculation of the equivalence ratio includes toluene.
0.01 Torr and melting point 239 °C [17]) was synthesized at TDA and used as the Pd precursor. Pd(THD)2 is a coordination complex, and as such the binding energy between Pd and THD is small. Upon heating, it dissociates readily, releasing a Pd atom. The precursor was dissolved in toluene (J.T. Baker 99.7% purity). The concentration of Pd(THD)2 in toluene solution was less than 1.9 wt% in the experiments.

The size distributions of Pd nanoparticles were measured at the reactor exit using a scanning mobility particle sizer (TSI SMPS 3090). A nominal flow of 0.3 L/min of the diluted exhaust was sampled into the SMPS. The residence time from the reactor exit to the SMPS inlet was 0.6 s, which is short enough to prevent coagulation of particles. The SMPS is composed of an electrostatic classifier (Model 3080) and a particle counter (Model 3025A). The classifier was equipped with a nano differential mobility analyzer (Model 3085). The diameter of the impactor nozzle was 0.0457 cm. The particle size distribution was scanned over the range of 4.5–160 nm in diameter. Each scan time took 55 s.

The particles were also collected on grids (Electron Microscopy Science HC200-CU) and analyzed by Transmission Electron Microscopy (TEM, Philips EM420). Each grid, affixed on top of an aluminum rod (0.6 cm in diameter) with aluminum tape, was exposed to a diluted exhaust stream flow parallel to the grid surface. The linear flow rate of the aerosol was 13 m/s over the grid. Under this condition, the flow is turbulent and the principal mechanism of particle collection is diffusion of the particles across the laminar boundary layer near the surface, which may bias against large particles. High-resolution TEM, STEM/EDX, and X-ray photoelectron spectroscopy (XPS) analyses of particle structure and chemical composition were carried out for particles from selected experiments. The details of the particle characterization are described elsewhere [18].

2.2. Procedure

Two different types of tests were performed as shown in Table 2. In the first type (Runs 3 and 4), the concentration of Pd(THD)2 was kept constant at 1.92 wt% in the atomizer, corresponding to ~4.5 × 10−4 moles Pd per mole CH4 in the main reactor flow. The furnace temperature was transient and increased at a constant rate of 20 K/min. This allowed us to determine the furnace temperature at the point of ignition with a specified catalyst condition. In the second type the furnace temperature was held constant, while the Pd(THD)2 concentration was transient and raised gradually, from 0 to 1.92 wt% until ignition was observed (Run 7). This allowed for determination of the minimum catalyst concentration for ignition at a specified furnace temperature. Additional experiments were carried out to measure baseline methane ignition under non-catalytic conditions (Runs 1, 2 and 6).

A key experimental challenge was to minimize the effect of wall deposits. The effect of the Pd deposited on the reactor wall was carefully investigated in Run 5. The test was carried out without the use of a Pd precursor but with a quartz tube repetitively used in prior catalytic experiments.

In addition, Runs 8 and 9 were designed to produce Pd/PdO nanoparticles for TEM sampling. To avoid fuel ignition, which results in large changes in gas temperature and concentration, methane was omitted from the O2/N2 flows, and their combined flow rate was equal to those of catalytic experiments. The mass loading of the Pd(THD)2 in toluene was 1.2 wt%, which is about the same as that in Run 7.

3. Detailed kinetic modeling

3.1. Mathematical descriptions

The underlying reacting flow problem was simulated as an initial value problem. SURFACE CHEMKIN [19] was utilized to solve the system of equations and to calculate the chemical reaction rates for both gas-phase and gas-surface processes. The model is capable of simulating the evolution of temperature and species along the flow axis. Simulations were performed at 1 atm pressure with and without a catalyst. Convective time t was obtained from the local linear gas velocity u and the axial position x of the flow reactor by the relationship, \( t = \int_0^x dx/u \). Since the flow reactor operates under the laminar flow condition, the flow is inherently two-dimensional; and the velocity profile is parabolic. Nonetheless, the current analysis assumes this to be a plug flow problem and neglects the radial transport – a simplification in comparison to the actual experiments. Sensitivity analyses, experimentally and computationally, were performed to examine this model assumption.

The gas-surface reaction rate constant is described as

\[
k = \gamma \sqrt{\frac{8k_BT}{\pi m_i}} \pi r_x^2
\]

where \( \gamma \) is the reaction probability or sticking coefficient, \( k_B \) the Boltzmann constant, \( m_i \) the molecular mass of ith gas-phase species, and \( r_x \) the particle radius. The species conservation is written as

\[
\frac{dY_i}{dt} = (\dot{\omega}_{g,i} + \zeta \dot{\omega}_{h,i}) \frac{M_{wi}}{\rho}
\]

Table 2

Summary of experimental condition and key results.

<table>
<thead>
<tr>
<th>No.</th>
<th>Experimental type</th>
<th>Flow condition of Table 1</th>
<th>Furnace temperature</th>
<th>Moles Pd/mole CH4</th>
<th>Median diameter, ( a ) (( \mu m ))</th>
<th>Surface-to-volume ratio, ( a ) (cm(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>Non-catalytic</td>
<td>F-1</td>
<td>1140</td>
<td>1077</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Run 2</td>
<td>Non-catalytic</td>
<td>F-1</td>
<td>1142</td>
<td>1073</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Run 3</td>
<td>Catalytic</td>
<td>F-2</td>
<td>998</td>
<td>970</td>
<td>4.3 × 10(^{-4} )</td>
<td>24</td>
</tr>
<tr>
<td>Run 4</td>
<td>Catalytic</td>
<td>F-2</td>
<td>954</td>
<td>916</td>
<td>4.7 × 10(^{-4} )</td>
<td>28</td>
</tr>
<tr>
<td>Run 5</td>
<td>Non-catalytic</td>
<td>F-1</td>
<td>1179</td>
<td>1117</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Run 6</td>
<td>Non-catalytic</td>
<td>F-1</td>
<td>1113</td>
<td>1113</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Run 7</td>
<td>Catalytic</td>
<td>F-2</td>
<td>973</td>
<td>973</td>
<td>2.1 × 10(^{-4} )</td>
<td>19</td>
</tr>
<tr>
<td>Run 8</td>
<td>No ignition</td>
<td>F-3</td>
<td>773</td>
<td>773</td>
<td>26</td>
<td>0.016</td>
</tr>
<tr>
<td>Run 9</td>
<td>No ignition</td>
<td>F-3</td>
<td>973</td>
<td>973</td>
<td>23</td>
<td>0.016</td>
</tr>
</tbody>
</table>

\( a \) Measured at the reactor exit.

\( b \) The reactor tube used was contaminated by wall coating.

\( c \) Molar loading, particle diameter and surface area at the point of ignition.
Where $y$ is the mass fraction, $M_y$ the molecular weight, $\rho$ the gas mass density, $\gamma$ the surface area-to-gas volume ratio of the catalyst, $\omega_k$ and $\omega_i$ are the gas-phase and gas-surface molar production rates, respectively.

The rate of temperature change in the reactor is obtained by considering the heat release due to chemical reactions in addition to the convective heating/cooling

$$\frac{dT}{dt} = \frac{dT_a}{dt} - \frac{1}{\rho c_p} \sum_i \left( \omega_{k,i} + \gamma \omega_{i} \right) h_{M_{y,i}}$$

where $h$ is the specific enthalpy, $c_p$ the specific heat capacity of the gas mixture. The first term on the right-hand side of the equation expresses the experimental temperature gradient obtained from a direct measurement for a non-reacting flow. As will be shown later, the particles formed are substantially smaller than the mean free path of the gas. Hence the particles are treated as being in free molecule regime. The time evolution of the site fraction $\theta_i$ for the $i$th surface is given as,

$$\frac{d\theta_i}{dt} = \frac{\omega_{i}}{\Gamma}$$

where $\Gamma$ is the catalytic surface site density.

### 3.2. Chemical kinetic models

The gas-phase reaction model employs USC Mech II [16]. The model was developed for H$_2$/CO/C$_1$–C$_4$ hydrocarbon combustion through a series of kinetic modeling studies over the last decade [16,20–29]. The model is composed of 784 reactions and 111 species, and has been validated over a variety of experiments including ignition delays, laminar flame speeds, and species profiles under the conditions relevant to the present flow reactor experiments.

The surface reaction mechanism was largely derived from the work of Jackson and coworkers [9,30,31]. The resulting model is shown in Table 3. It consists of five reversible and seven irreversible reactions with nine surface species. The total surface site density $\Gamma$ available for the catalytic reactions on a Pd particle was set to $\Gamma = 1.95 \times 10^{-9}$ mol/cm$^2$, i.e., the average of the literature values for the Pd/PdO phases [9,15,30–32].

The sticking coefficient of O$_2$ (R1f) and the surface coverage ($\theta_0$) dependent energy of desorption (R1b) are based on the temperature-programmed desorption (TPD) experiments [33]. These rate parameters values were also by Wolf et al. [9] and Jackson and coworkers [30,31]. The rate parameters of H$_2$O adsorption and desorption (R2f and R2b) were adopted from a reaction model by Deutschmann et al. [32], who studied catalytic ignition of hydrogen over a Pd catalyst in a stagnation flow burner. Cao and Chen [34] reported a Density Functional Theory (DFT) calculation for water adsorption on Pd [1 1 1]. The critical energies adopted in our model were taken from their DFT study.

The reactions and their rate parameters of R6–12 were taken mainly from Sidwell et al. [15]. The activation energy of dissociative adsorption of methane on oxide surface sites (R11) was reduced from 38 to 20 kJ/mol. This downward revision is supported by the theoretical result of Broclawik et al. [35,36]. Although a thermodynamically consistent approach [37] may be employed for assigning the surface reaction rate parameters, this was not attempted here because the exact mechanism for the surface reaction of CH$_4$ remains quite uncertain.

### 4. Results and discussion

#### 4.1. Reactor temperature profiles

Under the current experimental condition the flow inside of the reactor is laminar (568 $\gg$ Re $\gg$ 236). The resulting parabolic velocity profile creates a radial gradient in the gas temperature. In the axial direction, a temperature gradient also exists due to the finite time needed to equilibrate the gas flow with the wall temperature. For this reason, the gas temperature was measured both at the centerline $T_{center}$ and adjacent to the wall $T_{h,wall}$. In a pure N$_2$ flow at a rate equal to the ignition tests (see, mixture F-0 of Table 1). The results are presented in Figs. 3 and 4, respectively. The uncertainty for the temperature measurement is estimated to be $\pm 15$ K. As seen, the gas in the reactor undergoes heating in the first two-

---

### Table 3

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate parameters</th>
<th>Reference/comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1f</td>
<td>O$_2$ + 2Pd(S) $\rightarrow$ 2O(S)</td>
<td>$0.8^c$ $\times$ $10^{24}$</td>
<td>$-0.5$ 230–115$\theta_0$</td>
</tr>
<tr>
<td>1b</td>
<td>2O(S) $\rightarrow$ O$_2$ + 2Pd(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>[9,30,31,33]</td>
</tr>
<tr>
<td>2f</td>
<td>H$_2$O + Pd(S) $\rightarrow$ H$_2$O(S)</td>
<td>$0.75^c$</td>
<td>[32]</td>
</tr>
<tr>
<td>2b</td>
<td>H$_2$O(S) $\rightarrow$ H$_2$ + Pd(S)</td>
<td>$1.00$ $\times$ $10^{24}$</td>
<td>44</td>
</tr>
<tr>
<td>3f</td>
<td>H(S) + O(S) $\rightarrow$ OH(S) + O(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>94.5</td>
</tr>
<tr>
<td>3b</td>
<td>OH(S) + Pd(S) $\rightarrow$ H(S) + O(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>113.8</td>
</tr>
<tr>
<td>4f</td>
<td>H(S) + OH(S) $\rightarrow$ H$_2$O(S) + Pd(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>31.1</td>
</tr>
<tr>
<td>4b</td>
<td>H$_2$O(S) + Pd(S) $\rightarrow$ H(S) + OH(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>88.8</td>
</tr>
<tr>
<td>5f</td>
<td>2OH(S) $\rightarrow$ H$_2$O(S) + O(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>14.5</td>
</tr>
<tr>
<td>5b</td>
<td>H$_2$O(S) + O(S) $\rightarrow$ 2OH(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>32.8</td>
</tr>
<tr>
<td>6f</td>
<td>CO(S) $\rightarrow$ CO(S) + Pd(S)</td>
<td>$5.00$ $\times$ $10^{24}$</td>
<td>62.8</td>
</tr>
<tr>
<td>7f</td>
<td>CO(S) + O(S) $\rightarrow$ CO$_2$ + Pd(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>C(S) + O(S) $\rightarrow$ CO(S) + Pd(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>49</td>
</tr>
<tr>
<td>9</td>
<td>CH$_4$ + 2Pd(S) $\rightarrow$ CH$_2$(S) + H(S)</td>
<td>$4.00$ $\times$ $10^{24}$</td>
<td>196</td>
</tr>
<tr>
<td>10</td>
<td>CH$_2$(S) + 3Pd(S) $\rightarrow$ C(S) + 3H(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>85.1</td>
</tr>
<tr>
<td>11</td>
<td>CH$_2$(S) + Pd(S) + O(S) $\rightarrow$ CH$_2$(S) + OH(S)</td>
<td>$4.20$ $\times$ $10^{24}$</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>CH$_2$(S) + 3O(S) $\rightarrow$ C(S) + 3OH(S)</td>
<td>$5.13$ $\times$ $10^{24}$</td>
<td>25.1</td>
</tr>
</tbody>
</table>

---

*a* Arhenius parameters for the rate constants written in $k = A \times T_0^{x} \exp(-E/RT)$. The units of $A$ are given in terms of mol, cm$^3$/s. E is in kJ/mol.

*b* The surface coverage is specified as the site fraction $\theta$. Total site density of Pd is $\Gamma = 1.95 \times 10^{-9}$ mol/cm$^2$.

*c* Sticking coefficient.

$d$ The frequency factor was estimated from vibration frequency (10$^{13}$ s$^{-1}$) and scaled by the total site density $\Gamma$.

*e* The activation energies are based on the DFT results of Cao and Chen [34].

$f$ The reaction order is 1 for Pd(S).

*g* The sticking coefficient was taken from Sidwell et al. [15]. The activation energy was deduced from Broclawik et al. [35,36].
thirds of the reactor and cooling in the remaining section. As expected, the centerline and wall temperature profiles can differ from each other quite significantly, by as much as 200 K. Along the centerline the temperature rises more gradually than that close to the wall; and it reaches its peak value further downstream than the temperature adjacent to the wall. The delay in temperature rise is certainly caused by the finite heating rate under the laminar flow condition. In comparison, Fig. 4 shows that heating along the inner wall is more rapid and reaches the highest temperatures closer to the inlet than along the centerline.

The inhomogeneous temperature makes it difficult to interpret the data quantitatively. A realistic modeling approach would have to simulate the problem as a two-dimensional, laminar reacting flow problem. Because of the computational difficulties involved, this was not attempted in this study. Rather we used both the centerline and near-wall temperatures as the two limiting cases for one-dimensional numerical simulation.

### 4.2. Catalytic ignition

We first examine the test cases in which the furnace temperature increased at 20 K/min (Runs 1–4). The furnace temperatures, $T_{f1}$ and $T_{f2}$, at the point of ignition are recorded and shown in Table 2. The experiments were found to be reproducible (cf. Runs 1 and 2). The variations of CH$_4$ and CO$_2$ concentrations are presented as a function of the furnace temperature in Fig. 6. It is seen that at the point of ignition the CH$_4$ mole fraction drops quite abruptly while that of CO$_2$ rises accordingly. For the catalytic case, the rise of the CO$_2$ mole fraction prior to the disappearance of CH$_4$ was caused by oxidation of toluene. This oxidation process is seen to be gradual and non-explosive. Experimentally, we found that under non-catalytic conditions toluene itself did not affect methane ignition.
The results demonstrate that methane ignites noncatalytically at around 1100 K furnace temperature, corresponding to a maximum gas temperature of roughly 950 K along the centerline of the reactor. The use of catalyst generated in situ leads to a reduction of the furnace temperature by about 150 K at the point of ignition, using a Pd loading of ~0.025 cm\(^{-1}\) (catalyst surface area to total gas volume), as shown in Table 2. Under this condition, the atomic Pd to CH\(_4\) ratio is around 4.5 \(\times 10^{-4}\), corresponding to about 3 mg Pd/(g CH\(_4\)).

Runs 3 and 4 were designed to test the operation of the atomizer. In Run 3 the atomizer was covered by ice packs, reducing its temperature to ~278 K. For Run 4 the atomizer was operated at a somewhat higher temperature (283 K). This small difference in temperature was sufficient to change the loading of aerosol by 10%. The impact was captured by the experiment. With a higher catalyst loading (by about 10%), the furnace temperature at ignition was reduced by about 50 K, as shown in Table 2 and Fig. 6.

4.3. Particle size distribution

The particle size distribution functions (PSDFs) were determined at the exit of the reactor. Fig. 7 presents several PSDFs obtained during Run 3. These samples were collected with a dilution ratio of ~10 and an aerosol transmission time of 0.6 s. Since the number density of the particles is of the order of 10\(^8\) cm\(^{-3}\) at the exit of the reactor, this density drops to 10\(^7\) cm\(^{-3}\) after dilution. Assuming the coagulation rate constant to be the collision limit (\(\sim 10^{-9}\) cm\(^2\)/s), we find the characteristic coagulation time to be \(1/(10^7 \times 10^{-9}) \sim 100\) s. Hence, little to no coagulation losses are expected for the aerosol sampled.

As seen the median diameter of the particles falls between 20 and 30 nm. Without injecting the Pd(THD)\(_2\) precursor solution as an aerosol, the same measurement yields only a trace of particles with a number density similar to the ambient background. Although the particle diameters are mobility diameters, they should be very close to the true diameters for particles in the observed size range [38–40]. Over the period of 20 min during which the furnace temperature was increased, the PSDFs remained almost identical. This indicates that the precursor injection rate was steady, and that the processes of aerosol evaporation and precursor decomposition followed by particle nucleation and growth were independent of the temperature for \(T_f > 800\) K. It also suggests that these processes were complete or almost complete near the inlet region of the reactor and at temperatures substantially below the peak temperature of the gas.

All of the PSDFs observed are roughly log-normal with median diameter as expected for particle size growth dominated by particle–particle coagulation. Additionally, the tail towards the small size end of the distribution was also expected, and is indicative of persistent particle nucleation, perhaps due to the residue Pd vapor in the flow tube. The small shoulder towards the large particle size is probably indicative of the presence of aggregates. This behavior in PSDFs was commonly seen in homogeneous soot nucleation and growth [41–48], and is not indicative of particles produced from aerosol drying or breakup. Given the mass fraction of Pd(THD)\(_2\) in toluene and the initial aerosol droplet size, the particles would be about 100 nm in diameter if they were produced purely from toluene evaporation. If the particles were produced from a combination of aerosol drying and breakup, the size distribution would be significantly broader than observed.

The homogeneous nucleation mechanism for particle formation is also supported by second order of coagulation kinetics. If we start with Pd(v) as a monomer at a concentration of \(N_0 = 2 \times 10^{14}\) cm\(^{-3}\), uniformly dispersed in the gaseous reactant mixture, (calculated from the initial Pd(THD)\(_2\) loading for Runs 3 and 4) and assuming a unity sticking probability and a bimolecular coagulation rate constant of \(b = 1 \times 10^{-9}\) cm\(^3\)/s, we estimate that after 1 s, the number density of Pd particle is

\[
N \sim \frac{N_0}{1 + bN_0t} \sim 10^9 \text{ cm}^{-3}
\]

This is consistent with the observation shown in Fig. 8. In addition, the particle diameter may be estimated from the number of atoms in each particle \((\sim 2 \times 10^9)\) and an assumed mass density
of $10 \text{ g/cm}^3$. This gives a mean diameter of 20 nm, which is close to the experimental observation ($\sim 25$ nm). Of course, the initial non-uniform distribution of the aerosol could cause the local Pd(v) concentration to exceed the initial concentration of $2 \times 10^{14} \text{ cm}^{-3}$. This would result in an effectively shortened coagulation time for particle production.

The measured PSDFs can be fitted into a tri-log-normal distribution,

$$
\frac{dN}{d\log D_p} = \frac{1}{\sqrt{2\pi \log \sigma_k}} \exp \left\{ \frac{[\log(D_p/(D_{pk})]^2}{2(\log \sigma_k)^2} \right\}
$$

where $D_p$ is the particle diameter, $N_k$, $(D_p)_k$ and $\sigma_k$ are the number density, the median diameter, and the geometric standard deviation of the $k$th size mode, respectively. Fig. 8 presents a sample of the fit to data taken from Run 3. Aside from the fact that the PSDF parameters are roughly invariant with respect to the furnace temperature (especially the dominant, second mode), the most important feature here is that $\sigma_2 = 1.53$, which is slightly larger but close to that of a self-preserved distribution function of 1.46 \cite{49}. Hence, the particles measured are conclusively those from nucleation and growth out of the gas-phase precursors.

As we discussed earlier, the PSDFs are not sensitive to the temperature for $T_f > 800 \text{ K}$. Below that temperature, however, this is not the case. Fig. 9 shows that below 800 K the median particle diameter $(D_p)$ rises to 40 nm in some cases, whereas the surface area-to-volume ratio $\zeta$ (integrated from the distribution function) remains relatively constant. The rise in the median diameter at low temperatures was probably caused by coke formation or carbon deposition, since the aerosol was injected into the reactor in a nitrogen stream and locally the precursor flow was extremely fuel rich for a period of time. Meanwhile, toluene undergoes pyrolysis either homogeneously or catalyzed by dissociation of the Pd(THD)$_2$ and Pd/PdO clusters formed thereafter. Regardless, the observed variations in the median size below 800 K do not affect our interpretation of the experiment, since ignition was observed above that temperature.

4.4. Particle composition

To confirm that the particles observed are palladium and to examine the fine structure of these particles, we carried out TEM analysis on particles collected in Runs 8 and 9, in which the furnace temperature was held constant and equal to 773 and 973 K, respectively. Fig. 10 shows the TEM images from the two runs.
Both TEM grids were exposed to the exhaust flow for 6 min. The two images were almost identical; an observation consistent with the mobility size measurement. Most of the particles are smaller than the median diameter $D_{p,i}$ observed by SMPS. This could be due to the fact that the current particle collection mechanism relies on the particle diffusion towards the grid. The collection efficiency would be, therefore, biased against larger particles. More detailed particle structure and composition were probed by high resolution TEM and XPS, as described in a separate paper [18]. Only key results are summarized here. Fig. 11 shows HRTEM images collected for particles representative of the samples. The fact that the images show lattice spacings that clearly correspond to the Pd(1 1 1) interplane spacing indicates that bulk of the particles is crystalline, metallic Pd. XPS analyses, however, show that an oxide coating several atomic layers thick is present on the surface of the particles collected in the 973 K experiment. In the 773 K experiment, the particles have nearly identical bulk crystalline Pd structure, but almost no surface oxide [18]. This observation suggests that oxide growth is kinetically controlled, and that formation of the oxide may be a critical step in ignition, which occurs at 973 K, but not 773 K. This observation is consistent with the literature on oxide formation for bulk Pd surfaces over much longer residence time [8,9], and also with the observation that PdO is more catalytically active than Pd [2]. An appreciable amount of SiO$_2$ or partially oxidized silicon was also detected in the particle sample [18]. Control experiments show that the source of the silicon contamination was the toluene solvent used to dissolve the Pd(THD)$_2$ precursor. Because silica is a stable, chemically inert oxide, its participation directly in the catalysis process is quite unlikely. This is also because the Pd particles are relatively large. The presence of this silica contamination should not have much effect on the catalytic chemistry of the Pd particles. Indeed, noncatalytic runs with the toluene solvent only show the ignition temperature to be nearly identical to that without toluene injection.

4.5. Possible wall effect

SMPS, TEM and XPS evidence all points to a mechanism of ignition induced by the catalytic activity of the Pd/PdO nanoparticles produced in situ from the decomposition of the Pd(THD)$_2$/toluene aerosol. An issue that remains to be addressed is the role of condensed matter deposition on the wall and the subsequent wall catalysis. As we discussed earlier, it is nearly impossible to eliminate wall catalysis completely due to the finite surface-to-volume ratio of the reactor. Hence, our effort was directed at minimizing the effect of wall catalysis.

The precursor atomizer was designed specifically for that purpose. Because of the use of multiple impactors and hence the relatively small Stokes’ number, the aerosol follows the flow closely; and the droplets have little possibility to impinge onto the reactor wall before they disintegrate. In addition, the unburned reactant gas (CH$_4$/O$_2$/$N_2$) acts as a sheath surrounding the aerosol injection tube at the inlet of the reactor. This design further prevents the aerosol from reaching the reactor wall, at least before coming in contact with the unburned gas. Finally, as nanoparticles begin to form in the gas flow, the fact that the wall temperatures are higher than the centerline temperature means that thermophoretic effects tend to drive particles away from the walls. Under ignition conditions, heat release in the gas-phase may reverse this tendency to some extent, but because the experiments always were scanned from non-reactive conditions toward ignition, thermophoresis should help prevent catalyst deposition up to the ignition point, and thus the ignition temperatures or concentrations should not be strongly affected by wall catalysis. Nonetheless, there still remains a minor possibility that the actual ignition is induced by catalytic reaction on the reactor wall.

Fig. 11. HRTEM images of nanoparticles sampled in Run 8 (left) and Run 9 (right). The furnace temperature $T_f$ was kept at $T_f = 773$ K and 973 K, respectively. Most particles were found to be rich in Pd metal.

Fig. 12. CH$_4$ and CO$_2$ mole fractions measured during Run 5 as a function of the furnace temperature of Zone I, $T_{f1}$. The wall of the reactor tube used for Run 5 was contaminated by wall coating of condensed-phase material from Pd(THD)$_2$ decomposition.
To examine the influence of catalysis on the reactor wall independently, an experiment (Run 5) was carried out without injecting the Pd(THD)$_2$ precursor but using a quartz tube with a visible coating of catalyst from a prior experiment. Fig. 12 shows the CO$_2$ and CH$_4$ profiles as a function of the furnace temperature. It is seen that the “contaminated” tube caused the methane mole fraction to drop, starting at around $T_{f,1} = 730$ K. It reached a plateau at around $T_{f,1} = 1000$ K. Interestingly, the ignition occurs at $T_{f,1} \sim 1180$ K (Table 2), about 30 K higher than experiments conducted in clean, unused tubes (Runs 1 and 2).

We interpret the above observation as follows. In Run 5, wall catalysis indeed occurs, leading to the formation of the plateaus in the concentration profiles. Ignition at a furnace temperature $\sim 1180$ K is caused by the homogeneous process. A higher ignition temperature is caused by a reduced methane concentration due to catalytic conversion on the wall. Hence, it is clear that in this case wall catalysis actually retarded the ignition process. More importantly, the catalytic ignition studies in Runs 3 and 4 (Fig. 6) show constant CH$_4$ concentration over the entire temperature range up to the point of ignition. The absence of any significant drop in CH$_4$ concentration prior to ignition indicates that wall catalysis was indeed suppressed.

4.6. Mechanism of particle formation and catalytic activity

Summarizing the above results, we may now advance a phenomenological description of the particle formation mechanism and its catalytic activities. The kinetic processes of catalyst particle formation may be described by the following processes:

1. 1–10 μm-diameter toluene droplets containing Pd(THD)$_2$ vaporize, and the Pd(THD)$_2$ decomposes, generating Pd vapor or Pd clusters.
2. Pd(v) + Pd(v) $\rightarrow$ Pd$_2$.
3. Pd(v) + Pd$_2$ $\rightarrow$ Pd$_3$.
4. Pd$_2$ + Pd$_2$ $\rightarrow$ Pd$_4$.
5. ......
6. Pd$_i$ + Pd$_j$ $\rightarrow$ Pd$_{i+j}$.

This coalescence process leads to the formation of Pd nanoparticles, as observed in Figs. 7–11. The surface of the Pd particles becomes oxidized, especially for temperatures above $\sim 973$ K, leading to enhanced catalytic activity, which ignites the gas mixture at reduced temperature.

What remains unclear is why the oxide does not form at an early stage of cluster and particle formation. The reason may be thermodynamic and/or kinetic in nature. It is possible that for small particles the formation of palladium oxides is not favorable thermodynamically. A more plausible cause for the lack of bulk PdO formation is the finite time required to mix the reactants and diffuse oxygen to the surface. As the aerosol is injected into the reactor and undergoes evaporation and decomposition, this flow stream is not yet mixed locally with oxygen in the sheath. Hence the initial particle nucleation process takes place in spatial regions depleted of oxygen. If oxygen is present locally, it would have been depleted by toluene decomposition and oxidation, as evidenced by the early rise of CO$_2$ in Fig. 6. The burst of nucleation followed by coagulation causes the Pd(v) to condense onto existing particle surface rapidly, before the particles have an opportunity to mix by diffusion with the outer sheath of oxygen. The result is a particle with a Pd core that oxidizes slowly at low temperatures, and forms a real oxide layer only near or above $\sim 973$ K, as confirmed by TEM and XPS results. Although additional work at the elementary level is needed to confirm the above analysis, we are now in a position to advance a chemical model to explain the ignition phenomenon observed.

4.7. Detailed kinetic modeling

To facilitate model comparison, Runs 6 and 7 were made, in which the furnace temperature was held constant. These runs were necessary because we were able to measure the temperature pro-
files along the reactor only under the condition of steady reactor operation. Under the condition of transient furnace temperature, the rise in the gas temperature lags further behind as compared to the temperature profiles obtained under steady operating condition and shown in Figs. 3 and 4. For this reason, while the results of Runs 3 and 4 are useful for examining the response of methane ignition to furnace temperature, they cannot be modeled with certainty.

For background, noncatalytic ignition of methane (Run 6), we increase the furnace temperature in 5 K steps. The reactor was allowed to equilibrate for 30 min at each furnace temperature, until ignition is observed. For the mixture composition given as $F=1$ in Table 1, the ignition was observed at $T_f=1113$ K with an uncertainty of $\pm 5$ K. This temperature is about 35 K lower than that of Runs 1 and 2, which is reasonable considering that the furnace temperature is transient in those runs. In run 7, the furnace temperature was held fixed at 973 K. The Pd(THD)$_2$ loading was increased gradually while the Pd particle size distribution was measured continuously. Fig. 13 shows selected PSDs data at various times over the course of the run. The median diameter observed continued to increase, as seen in Fig. 14, while the total number density remained nearly the same over the 20-min experiment period. When the catalytic loading reached $1.3 \times 10^{-2}$ cm$^{-1}$, i.e., the highest loading shown in Fig. 13, ignition occurred. At that point, the atomic Pd-to-CH$_4$ ratio was $2 \times 10^{-4}$ and the surface area-to-gas volume ratio $\zeta$ was 0.013 cm$^{-1}$, as shown in Table 2. As before, the PSDs are trimodal and the main mode is log-normal. This set of the experiments was reproducible, and was used as the basis of modeling studies in what follows.

To verify the accuracy of USC Mech II for gas-phase methane oxidation under conditions comparable to the current flow reactor experiments, we first report the simulation results and compare them to the turbulent flow reactor data of Hunter et al. [50]. In those experiments, methane was highly diluted and oxidized in an air-like mixture at pressures of 6 and 10 atm. The temperature along the reactor axis was nearly constant and ranged from 950 to 975 K. As shown in Fig. 15, major and minor species concentrations were predicted by USC Mech II accurately.

Additional computational cases are summarized in Table 4. Simu-1 and -2 correspond to Run 6 and Simu-3–6 represent Run 7. In these simulations, the measured background temperatures (Figs. 1 and 2) were used as a model input, i.e., the first term on the right-hand side of Eq (3). Heat release is accounted for in the second term of that equation. Of course, this description is not

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig14}
\caption{Particle median diameter ($D_p$) and area-to-volume ratio $\zeta$ measured at the exit of the flow reactor during Run 7. Round and rectangular symbols represent ($D_p$) and $\zeta$ (STP), respectively.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig15}
\caption{Experimental (symbols [50]) and computed species profiles during homogeneous, non-catalytic oxidation of methane in a turbulent flow reactor. Left panels: 0.02CH$_4$–0.205O$_2$–0.775N$_2$ at 6 atm and $\sim 953$ K; middle panels: 0.02CH$_4$–0.205O$_2$–0.775N$_2$ at 10 atm and $\sim 953$ K; right panels: 0.021CH$_4$–0.205O$_2$–0.774N$_2$ at 6 atm and $\sim 974$ K.}
\end{figure}
mathematically rigorous since local heat release would affect the first term because of sensitivity of heat conduction and convection towards local temperature. This uncertainty, however, is expected to be smaller than the non-uniform temperature in the reactor. In the simulations, we used both the measured centerline and near-wall temperatures as model input and treated them as the two limiting cases.

Table 4 shows that the predicted furnace temperature at which the ignition occurs is only 14 K higher than the experimental value when the centerline temperature was used as a model input (also, see Fig. 16). Considering all of the experimental and model uncertainties, the close agreement is perhaps fortuitous, but encouraging nonetheless. If the near-wall temperature was used in the simulation, the furnace temperature of ignition was predicted to be 74 K lower than the observation. The results computed with the two limiting temperatures bracket the experimental value, as expected. Considering that the wall quenching of the free radicals was not considered in either computational case, the current results are considered as more than acceptable. In what follows, only computations made with the centerline temperature will be discussed, though computational results using the near-wall temperatures are reported in Table 4 for all cases.

Fig. 16 shows the CH4 and CO2 mole fraction profiles computed as a function of the furnace temperature, comparing the non-catalytic case (Simu-1) with the catalytic cases (Simu-3 and -5). Also shown in the figure are the corresponding experimental values. As seen, the computed temperatures are within 20 K of the experimental values. Under comparable conditions, the model predicts a reduction of 171 K in the furnace temperature at a catalyst loading of 2 × 10−4 (atomic Pd-to-CH4 ratio) and a corresponding surface area-to-gas volume ratio of 0.013 cm−1, whereas the experimental values give 140 K. The simulation results are expected to be sensitive to the local temperature inside the flow reactor, but since this temperature is not a constant, it was not easy to quantify this sensitivity.

Because toluene is used as the solvent for Pd(THD)2, its impact on the gas-phase reaction kinetics is considered in the simulation. USC Mech II predicts the laminar flame speed and ignition delay of toluene-oxidizer mixtures reasonably well [51]. However, the model includes a limited number of reactions for toluene oxidation under the current experimental conditions. Hence, the simulation was conducted by assuming all of the carbon in toluene was converted to CO2 (Simu-3) and by assuming all of the toluene remains as the reactant at the onset of the reaction (Simu-5). Unlike the experimental observation, Simu-5 did not yield noticeable toluene consumption prior to ignition, as seen in Fig. 16. The reason, of course, is gas-phase reactions and/or catalytic processes not accounted for by the model. On the other hand, the computed ignition temperature is not at all sensitive to the toluene chemistry, because Simu-3 and 5 yielded basically the same results. Overall, the combined gas-phase and gas-surface model predicts the experimental results well.

### 4.8. Mechanism of methane ignition catalyzed by Pd particles

Analysis of the computational results indicates that the ignition process involves both thermal and radical runaway. Fig. 17 presents the evolution of gas-phase species concentration and catalyst surface coverage just before ignition (Simu-3) against the axial position of the flow reactor and the reaction time. The model predicts the surface to be nearly saturated by O(S), in agreement with the XPS results at 973 K. For the reactor conditions used in Simu-3, the concentration of O(S) was found to be independent of the initial surface composition. Simulations by assuming the initial Pd surface being fully Pd(S) or fully saturated by O(S) yielded virtually identical ignition temperatures. Additional tests were made by introducing the Pd particles at different reaction times. The results show that as long as the particles were “injected” computationally in the first half of the reactor, the computed ignition temperature remains the same.

As seen in Fig. 17, the initial rise in temperature is caused by heating of the gas by the furnace until about 30 cm from the inlet. The subsequent rise in temperature is largely the result of heat release due to catalytic reactions. This may be seen in the top panel.
of Fig. 17 by comparing the centerline temperature profiles between the background and catalytic oxidation. From 50 to 60 cm, almost all CH₄ consumption and CO₂ production is the result of catalysis. At the same time, the reaction becomes autocatalytic, in that the temperature rise causes an increase in the catalytic reaction rate. At about 70 cm from the inlet, the temperature is brought to \(\approx 1000 \text{ K}\), at which point the increased desorption of oxygen leads to a rapid rise in other surface sites and the overall reaction rate. The temperature now increases rapidly. Above 1000 K, gas-phase reaction starts to play a role, as evidenced by the rapid rise in the gas-phase H, O, OH, and HO₂ concentrations.

To understand the impact of surface reactions on ignition, we carried out sensitivity analysis for the simulation discussed above. The sensitivity coefficient defined as 

\[
\frac{\Delta T_{\text{ig}}}{T_{\text{ig}}} = \frac{\text{change in temperature of ignition resulting from perturbing the pre-factors by a factor of 2}}{\text{average before and after perturbation}}
\]

The results are shown in Fig. 18. It is seen that the key steps are adsorption and desorption of O₂ (R1) and the oxidative dissociation of CH₄ on a vacant site (R11). These results are in agreement with what Fujimoto et al. [13] reported for CH₄ oxidation from 500 to 800 K over PdO surfaces. The overall catalytic reaction rate appears to be limited by this reversible adsorption and desorption process, which controls the density of vacant Pd sites needed for CH₄ oxidative dissociation on catalyst surfaces. Water or OH poisoning is predicted to play a minor role under the conditions studied. Around 900 K, the major pathway for water formation is the surface metathesis reaction between two surface OH sites.

The numerical results reported in Fig. 17 are complicated by the variable centerline temperature. To better understand the ignition mechanism, we carried out calculations for stoichiometric methane oxidation in air under the adiabatic and isobaric conditions at an initial temperature of 900 K and 1 atm pressure. The computed temperature–time histories are shown in Fig. 19. The calcu-
lution for catalytic oxidation used typical Pd loading and size, i.e., \( D_p = 19 \) nm and the surface-to-volume ratio equal to 0.013 cm\(^{-1}\) (STP). Under this Pd loading, the ignition delay time is shortened by about two orders of magnitude compared to homogeneous, non-catalytic methane oxidation. For the catalytic case, analysis shows that the initial temperature rise at around \( 10^{-2} \) s is entirely caused by heat release from catalytic reactions. Interestingly the temperature levels off at around 1400 K just before it takes off again some \( 10^{-2} \) s later. This behavior is explored in detail, as shown in the inset of Fig. 19. Without considering gas-phase reactions, the predicted temperature plateaus at around 1400 K, far below the adiabatic flame temperature. In other words, the catalytic reaction shuts itself off at that temperature because surface desorption of \( \text{O}_2 \) becomes so rapid that the catalytic activity is lost. Yet because the catalytic reactions had brought the gas temperature to \( \sim 1400 \) K, close to the cross-over temperature of \( \text{H} + \text{O}_2 \) chain branching and termination under that pressure, homogeneous gas-phase reactions become active. Eventually ignition occurs because of both gas-phase thermal and radical runaways. Hence, the present analysis suggests a two-step process to ignition. That is, catalytic reactions result in initial heat release and raise the gas temperature. Although the temperature rise would shut off the catalytic activity at some point, gas-phase radical chain branching takes over eventually and completes the ignition process.

To assess the influence of initial temperature on the ignition delay time, we extend the above calculation to a range of 700–1500 K. Fig. 20 shows that under the level of Pd loading discussed earlier, the ignition delay time is shortened by two orders of magnitude from 700 to about 1200 K. When the initial temperature is at least 1400 K, the catalytic and noncatalytic ignition delay is identical because the catalyst activity is suppressed for reasons already discussed and also because gas-phase reaction kinetics tend to dominate at high temperatures. Over the range of temperature shown in Fig. 20 and up to 40 atm pressure (results not shown here), the ignition mechanism remains the same. That is, we observe a sequential, two-step process in which catalytic reaction dominates initially, but gas-phase reactions take over after catalytic processes are deactivated by the rising temperature.

5. Conclusions

Freely suspended palladium nanoparticles were generated in situ in a laminar flow reactor from an aerosol composed of \( \text{Pd(THD)}_2 \) diluted in toluene. Mixing the aerosol with a stream of methane, oxygen, and nitrogen (equivalence ratio \( \phi \sim 0.5 \)) under a heated condition can lead to a notable reduction in the ignition temperature of the unburned mixture, compared to homogeneous methane oxidation without palladium particles. Measurement of the particle size distribution shows that the median particle diameter is around 20 nm, and the surface-to-gas volume fraction is \( \sim 0.02 \) cm\(^{-1}\) (STP). The observed size distribution is consistent with a particle formation mechanism dominated by homogeneous nucleation and particle size growth by coagulation. TEM/XPS analysis shows that the particles have a crystalline palladium core and a few atomic layers of \( \text{PdO} \) on the particle surface for particles observed near or above 973 K furnace temperature, but very little oxide was formed at 773 K. Coupled with the observation that cat-

---

Fig. 18. Sensitivity coefficients, \(-\Delta T_{ig}/\tau_{ig}\), computed for Simu-3. A positive sensitivity coefficient indicates lowered ignition temperature. Reactions with noise-level sensitivities are omitted.

Fig. 19. Temperature–time histories computed for a stoichiometric methane/air mixture under adiabatic and isobaric conditions, showing the difference in ignition onset between catalytic and noncatalytic ignition of the mixture with initial temperature \( T_0 = 900 \) K and pressure \( p = 1 \) atm. The catalytic case used a median particle diameter \( D_p = 19 \) nm and the surface-to-volume ratio \( \zeta \approx 0.013 \) cm\(^{-1}\) (STP). The inset also shows the temperature history computed without considering gas-phase reactions.

Fig. 20. Ignition delay time computed as a function of initial temperature of a stoichiometric methane/air mixture under adiabatic and isobaric conditions. The catalytic case used \( D_p = 19 \) nm and \( \zeta \approx 0.013 \) cm\(^{-1}\) (STP).
alytic ignition occurred near 973 K, Pd oxidation kinetics must play a critical role in the catalytic process.

Numerical simulation using a detailed, combined gas-phase and gas-surface reaction model shows that the experimental results are well captured by the model. Simulation results suggested that the surfaces of Pd nanoparticles give rise to catalytic reactions at a temperature which would otherwise not lead to substantial gas-phase reactions. The heat release resulting from catalysis eventually brings the gas to a temperature where the catalytic reaction is overtaken by the gas-phase reactions, which eventually leads to thermal and radical runaway and fuel ignition.

The key surface reaction steps were found to be the reversible oxygen adsorption/desorption, which governed the vacant Pd site density and the overall rate of the catalytic reaction. Methane oxidative dissociation on a vacant Pd site is the rate-limiting step for catalytic conversion of methane to CO and hence the heat release.

Acknowledgements

The Utah and USC groups gratefully acknowledge support for this work from the Air Force Office of Scientific Research through the MURI program (FA9550-06-1-0400). The Utah, USC, TDA, and Reaction Systems efforts were also supported by AFOSR STTR contracts (FA8650-06-C-2673 and FA9550-07-0106) to TDA, with subcontracts to Utah and USC. In addition, the authors thank Mr. Brian Windecker of TDA Research for design and assembly of the catalyst test apparatus.

References