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Kinetics of catalytic oxidation of methane, ethane and propane over palladium oxide

Yuxuan Xin[a], Hai Wang[b], Chung K. Law[a,c,*]

[a] Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA
[b] Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA 90089, USA
[c] Center for Combustion Energy, Tsinghua University, Beijing 100084, China

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ABSTRACT

Catalytic oxidation of methane, ethane and propane over a palladium oxide (PdO) surface was investigated experimentally by wire microcalorimetry. The oxidation rate was determined for each reactant at atmospheric pressure in the temperature range of 600–800 K. The apparent kinetic parameters were extracted from the experimental measurements. It is shown that the oxidation of these hydrocarbons over the PdO surface proceeds with a similar mechanism: they undergo dissociative adsorption followed by the conversion of surface fragments to final products. A detailed surface reaction model is proposed, and the kinetic parameters of the crucial reactions are deduced from the present experimental observations. The catalytic oxidation rates are found to increase in the order of methane, ethane and propane. This observation is consistent with density functional theory calculations and may be correlated with the C–H bond energies of the corresponding surface intermediates.

1. Introduction

Freely-suspended catalytic nanoparticles were recently suggested to be a possible solution to reduce the ignition delay time of methane at temperatures substantially below where gas-phase radical-chain branching is the dominant mechanism of thermal and radical runaway. In particular, Shimizu et al. [1,2] examined the oxidation of methane-air mixture assisted by palladium (Pd) nanoparticles generated in situ from a soluble precursor in a flow reactor. They reported a two to three order of magnitude reduction in the ignition delay compared to homogeneous ignition. Catalytic combustion of methane has been extensively studied also for power generation from natural gas and pollution emission control, with numerous reviews in the literature [3–5]. Pd-based catalyst is recognized as the most active for methane oxidation, and several surface reaction models have been proposed [6,7], identifying several key issues [3] including Pd/PdO equilibrium, methane activation, water desorption and catalyst–supporter interaction. The rate-determining step is generally thought to be the initial cleavage of the C–H bond over a Pd surface site surrounded by Pd–O sites [8–10]. In addition, desorption and adsorption of oxygen plays a critical role because the rate of methane dissociative adsorption relies on the ratio of Pd and Pd–O sites [3]. Below around 900 K and under the fuel lean condition, the oxidized Pd state is favored thermodynamically [11].

The kinetics of catalytic oxidation of ethane and propane has been examined over a Pd foil [8] and supported Pd catalysts [9]. The reaction rates generally exhibit approximately zeroth and first order dependency with respect to the partial pressures of oxygen and the hydrocarbon, respectively, especially under fuel-lean conditions. Moreover, a series of Density Functional Theory (DFT) studies were reported by Weaver et al. [12–14] on the reactions of methane, ethane and propane over a PdO (101) surface. They identified a similar precursor-mediated mechanism and confirmed that dissociative adsorption is the rate-determining step. The energy barriers of this reaction step were reported to be 64.2 and 51.8 kJ/mol for methane and propane, respectively. Compared to methane, the reduced energy barrier to the dissociative adsorption of propane is consistent with its smaller C–H bond energies than that in methane.

Kinetic [8,9] and DFT [12–14] studies on ethane and propane oxidation over PdO consistently suggest a reaction mechanism similar to methane, that is, the activation of the hydrocarbon reactant over the catalyst surface acts as the rate-determining step. However, the rate coefficients for the activation of ethane and propane remain unavailable. Previously, catalytic oxidation of methane over a PdO surface has been examined using wire microcalorimetry [15,16]. It was shown also that under suitable experimental conditions, the rate coefficient of methane dissociative adsorption can be derived quite conveniently from wire

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* Corresponding author at: Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA.
E-mail address: cklaw@princeton.edu (C.K. Law).

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microcalorimetry [17]. We extend herein the work of [17] to ethane and propane, thereby providing a hierarchical kinetic investigation for the catalytic oxidation of alkanes up to propane over a PdO surface. Specifically, the overall reaction order with respect to the hydrocarbon reactant concentration and the apparent oxidation rates were determined within the pseudo-first order regime and under dilute conditions where the diffusion limitation is negligible and the overall reaction is controlled by the concentration of the hydrocarbon reactant and its surface reactions. The rate coefficient for the elementary dissociative adsorption of ethane and propane were also derived from the experimental data at the ambient pressure and over the temperature range of 620 and 740 K and compared to that of methane under similar conditions.

2. Experimental and simulation methods

2.1. Wire microcalorimetry

Wire microcalorimetry method has been described in detail elsewhere [15–19]. Briefly, the method quantifies the rate of surface reaction by measuring its heat generation. The experiment is performed over a catalytic metallic wire, which is resistively heated. The wire temperature is first increased to a certain value in a non-reactive gas such as nitrogen. When the system reaches steady state, the power input compensates the heat loss from the wire to the environment, and is recorded as the reference value. Afterwards, the test reactive mixture is introduced in the chamber and the wire is heated to the same temperature. Because the energy loss from the wire to the environment is the same for the reactive and non-reactive cases, the difference in their power input, Δp, is the heat generated by the surface reaction. The heat release rate is converted to the reaction rate by considering the enthalpy change of the surface reactions.

In the present study, a palladium wire 10 cm in length and 0.1 mm in diameter (99.99%, Aldrich) acts as the catalyst surface and gases of methane, ethane, propane, oxygen and nitrogen were used as the reagents. For each hydrocarbon reactant three reactive mixtures were prepared in a 5.0 l stainless steel chamber with the compositions of 1–3% CH_4, 0.5–1.5% C_2H_6 and 0.4–1.0% C_3H_8 in air. The chosen gas mixtures cover typical fuel-lean conditions with equivalence ratios ranging from 0.1 to 0.3, well below the flammable limit at atmosphere pressure. Under this condition, homogeneous gas-phase reactions are minimally activated.

2.2. Simulations

The natural convection flow generated around the catalytic wire is weak and well defined. To account for external molecular diffusion effects, the flow field was simulated using the commercial code FLUENT. Because of the large length-to-diameter aspect ratio of the wire, the gas phase composition and surface temperature are assumed to be constant in the axial direction of the wire. The simulation employs an axisymmetric, two-dimensional model on the cross section of the wire, as discussed previously [15–17]. The physical size of the simulation is 70 times the wire diameter, where room temperature, atmosphere pressure and fresh, quiescent reactant mixture are imposed as the boundary conditions. The catalytic wire was considered as a smooth cylinder with a given surface temperature, T, where surface reactions occur leading to heat release. As will be discussed later, the real wire surface is however far from smooth, and the increase in the surface area will be quantified. Diffusion of the reactants and products through the surface pore layer was not considered since such a treatment requires a detailed knowledge of the internal pore structure, which is not examined here. Experimental data for which pore diffusion is expected to play a role are excluded from kinetic parameter determination, as will be discussed later.

Gas phase chemistry is generally unimportant for the present experiments, but its effect is nevertheless considered in the detailed simulation. The reaction model is described by the 111-species and 784-reaction USC Mech II [20]. The surface chemistry for methane oxidation over PdO was extended from a model reported earlier [17], with reactions relevant to ethane and propane proposed herein. The thermochemical properties of the surface species were derived from the vibrational frequencies of surface species [21,22].

3. Results and discussion

3.1. Surface characterization

In an oxidizing environment at the temperature of interest, the surface of the Pd wire becomes fully oxidized. The oxidation process leads to a significant change in the morphology and composition of the wire surface. Several techniques may be applied to probe the catalyst surface [15], including Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX). Typical wire surfaces after experiments are shown in Fig. 1. These surfaces are characterized by a porous PdO layer. The pore size is distributed log-normally and has a median radius $\langle r \rangle = \sim 0.5\ \mu m$ and geometric standard deviation of 1.62. The surface density of the pore is approximately 0.1 μm^{-2}. The wire was pre-treated by a standard procedure [15]: heating at 923 K in N_2 followed by an exposure to a 2% CH_4/air mixture for 1 h. After this treatment, the morphology of the wire surface remains stable, allowing experiment to be conducted in a reproducible manner. As discussed in [17], atomic force microscopy revealed significant islands and crystal grains and steps on the wire surface. As a result, the actual surface area of an untreated wire is 1.7 times that of an ideal cylinder. Furthermore, wire microcalorimetry experiments below 670 K showed that the catalytic reaction on a wire treated by the above procedure is around a factor of two faster than on an untreated, fresh wire. Combining these two measurements, we estimated the surface area ratio of the treated wire to a perfect cylinder to be 3.5.

3.2. Heat release rate and apparent kinetic parameters

Figure 2 presents the heat release rates measured for the oxidation of methane, ethane and propane, over the temperature range of 540–800 K. Within this temperature range, the surface reaction rates are large enough to be probed by wire microcalorimetry while gas-phase reactions are suppressed. For each hydrocarbon reactant, three equivalence ratios were investigated. Figure 2 provides also a comparison of the reactivity of the three hydrocarbons with a similar carbon concentration. Clearly, the reaction rates decrease in the order of propane, ethane to methane. Figure 3 shows the reactant consumption rates, ω, derived from the measured heat release rate, Δp, the surface area ratio of 3.5 and the enthalpy of combustion, $\Delta_r H_m$. For the hydrocarbons tested, the onset of heat release was observed to occur at the same temperature (550 K). Above this temperature the heat release rates rise quickly.

Apparent kinetic parameters of the overall oxidation process can be derived from the surface reaction rates observed above 620 K. The unity reaction order has been observed in previous studies [8,9] and verified in this work, as shown in Fig. 4. The results are presented in Fig. 5 as a function of temperature. As expected, the reaction order of the hydrocarbon reactant was found