Some Critical Issues in the Analysis of Partial Oxidation Reactions in Monolith Reactors

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Abstract

In the catalytic oxidation of ethane on platinum-containing monoliths, the high rates of the surface reactions coupled with their high exothermicities lead to a very large axial temperature gradient over a distance comprising only a minor fraction of the reactor length. The temperature reaches a level such that homogeneous gas-phase reactions occur rapidly enough to make a large contribution to the overall conversion occurring in the remainder of the reactor. The gas temperatures generated by the surface reactions are high enough so that ignition delay times for the gas-phase reactions are small compared to total residence times in the reactor. For a quantitative assessment of the extent to which homogeneous gas-phase reactions contribute to the overall conversion, the most important considerations are having a reliable estimate of the temperature gradient generated by the surface catalyzed reactions at the front of the reactor and being careful to utilize a kinetic scheme for the gas-phase reactions that is appropriate for the reaction conditions.

1. INTRODUCTION

In the oxidative dehydrogenation of ethane on a platinum-containing monolith, much of the overall conversion of ethane is due to gas-phase reactions[1]. When ethane and oxygen come into contact with a monolith at a temperature of about 573 K, rapid oxidation of ethane to H_2O, CO, and CO_2 occurs on the surface of the platinum. The heat released by these reactions increases the temperature markedly. In a typical situation, the temperature increases to a level of 1123-1173 K at a distance through the monolith where only about one-fifth of the ethane has been converted. At these temperatures, the rates of homogeneous gas reactions become high enough for them to be responsible for virtually all of the remaining conversion of the ethane along the monolith. The production of ethylene and acetylene is attributed almost exclusively to reactions occurring in the gas phase. The heat required to sustain the endothermic dehydrogenation reactions yielding these products in the tail end of the reaction zone is supplied by exothermic gas-phase oxidation reactions that form additional H_2O and CO.

Existing information on the kinetics of homogeneous gas-phase reactions involved in the high-temperature oxidation of hydrocarbons is very extensive, and complex kinetic networks applicable to a number of different hydrocarbons have been developed[2-8]. For a specific application, the most general network possible on the basis of existing kinetic information may well be far more complex than is necessary for the purpose at hand. Consequently, it has become the practice to utilize simpler networks that are applicable to particular hydrocarbons or hydrocarbon mixtures and to particular ranges of reaction

conditions. This is important from the standpoint of utilizing computational resources efficiently. However, one must be very careful to utilize a network that is adequate for the problem under consideration.

In the oxidation of a relatively simple hydrocarbon such as ethane, the most general network available is clearly not needed. Nevertheless, in assessing the degree to which homogeneous gas-phase reactions contribute to the overall conversion of the ethane, one must be confident that the kinetic description is capable of making a reliable estimate of the ignition delay times. This, coupled with a satisfactory calculation of the rate of heat evolution and the corresponding axial temperature gradient in the front section of the monolith, is crucially important for addressing the problem.

2. RESULTS

An important feature of partial oxidation reactions in monolith reactors is that most of the conversion of reactants occurs in a very short time[9]. Despite the high temperatures involved, reactor contact times (which are frequently less than about 10 ms) are generally insufficient to bring the mixture into thermodynamic equilibrium. Figure 1 illustrates this by comparing experimental measurements with equilibrium calculations (C_2H_6/O_2=1.2, 1.2 atm, 1225 K, 20% N_2 dilution). Selectivities of conversion of ethane to the most abundant product species are shown. Oxygen is always totally consumed by the reactions and ethane conversions are high. This figure shows that while equilibrium favors the formation of synthesis gas and some methane, significant amounts of ethylene, acetylene, and water are produced. Irrespective of whether the observed products arise from surface-catalyzed or gas-phase reactions, these results indicate that a quantitative assessment of product composition requires a kinetic description that adequately accounts for intermediate products that would be only minor components at conditions of thermodynamic equilibrium. The partial oxidation experiments clearly reflect this by yielding ethylene, acetylene and water as such products. Given sufficient time, these products could be transformed to H_2 and CO by steam reforming reactions. The presence of water in the products is also an indicator of the high temperatures that develop within these reactors and therefore of the potential involvement of gas-phase reactions.
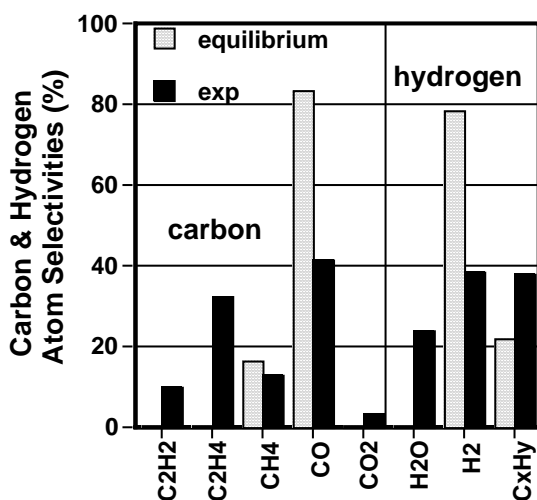
Figure 1. Comparison of experimental and equilibrium carbon and hydrogen atom selectivities (C_xH_y represents sum of C_2H_2, C_2H_4, and CH_4)
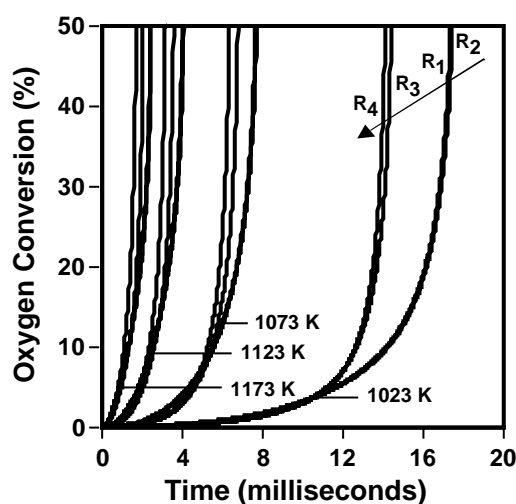
Figure 2. Ignition delay times for various reaction networks and temperatures (Networks R_1, R_2, R_3, and R_4 described in text)

The ignition delay time derived from a reaction network involving free radical intermediates provides a useful diagnostic for assessing the potential involvement of gas-phase reactions. It can be conveniently defined as the time required under adiabatic conditions for the reactions to consume some substantial fraction (say one-half) of the oxygen for given initial conditions of temperature and composition. If this time is shorter than the total residence time in the monolith, then there is a chance that gas-phase reactions may contribute to the conversion process. Figure 2 shows plots of oxygen conversion versus reaction time for various initial temperatures. Results of calculations using networks of varying complexity are included. Times calculated for 50% oxygen conversion are very reasonable measures of ignition delay times since chain reactions rapidly consume the remaining oxygen under the hydrocarbon-rich conditions of interest in partial oxidation. These conversion-time plots are obtained from adiabatic plug-flow calculations at partial pressures that are typical of catalytic experiments employing platinum monoliths (C_2H_6/O_2=1.2, 1.2 atm, 20% N_2). The selected temperatures also represent typical values measured at the outlet of partial oxidation reactors, with 1023 K being a lower limit.

Figure 2 shows that ignition delay times decrease rapidly as temperature increases. They drop from about 15 to 3 ms as the temperature is raised from 1023 K to 1173 K. For temperatures greater than about 1073 K, the ignition delay times are lower than typical residence times in the catalytic monoliths (~10 ms) and the possibility that gas-phase reactions contribute to the conversion is high. Although these ignition delay time calculations provide valuable guidance, they do not represent exactly the delay times in the monoliths. In the monolith, the exothermic surface-catalyzed steps are responsible for the temperature rise that speeds up the ignition process in the gas phase. This catalyst-assisted gas-phase ignition occurs under conditions of partial pressures and heat evolution that differ from those that apply in the absence of a catalyst. As described in further detail later, a proper assessment requires that surface and gas-phase reactions be simultaneously included in the analysis to account correctly for the resulting composition and temperature profiles.

Figure 2 displays ignition delay times for four free-radical reaction networks. R_1 and R_3 correspond to networks taken directly from the literature. R_1 is from Mims et al.[2] (115 species and 447 reactions). R_3 is from Curran et al.[3] (1034 species and 4238 reactions). While the former network includes hydrocarbons up to C_4 species only, and was assembled to study secondary reactions of ethylene in an oxidative environment, the latter includes up to C_8 hydrocarbons and was assembled to study oxidation of fuels in automotive applications. The ignition delay times calculated with these networks differ by only 20%. This level of agreement instills confidence that one can make a very reliable assessment of the contribution of gas-phase reactions. The comparison is included here to highlight the importance of selecting gas-phase networks that are complete enough for the conditions of composition and temperature under study. For practical reasons, gas-phase networks are commonly developed for limited regions of composition and temperature, and their predictive accuracy can be severely compromised if they are used outside their limits of validity. Thus, for example, reaction networks that are developed specifically for combustion or pyrolysis situations will generally not perform well under partial oxidation conditions. This is an issue of great importance because the inability of a network to capture ignition delay times and kinetic trajectories quantitatively can lead to erroneous conclusions about the role of the gas-phase reactions in situations like the one addressed here.

The use of gas-phase networks containing a large number of species can sometimes unduly stress the limits of computational resources. The analysis of experimental data frequently requires estimates of certain parameters. Such an analysis can become prohibitively long when a large number of material balance equations have to be integrated repeatedly in time or space as required by minimization procedures. Since in many situations a relatively small set of reactions is adequate for a description of the system, there is no need to include all the species in the calculations. Network reduction via formal optimization algorithms is of great utility here in providing a means for lowering the number of species and reactions without adversely compromising the integrity of the network[10]. This is illustrated in Figure 2, where ignition delay times are presented for networks R_2 (45 species,

234 reactions) and R_4 (47 species, 237 reactions), which correspond to reduced versions of the parent networks R_1 and R_3, respectively. Corroborating the adequacy of the network reduction procedures for the conditions at hand, both R_2 and R_4 accurately capture the ignition delay times obtained from the extended networks R_1 and R_3, respectively.

Figure 3 illustrates calculated pressure and temperature profiles for a typical situation in ethane partial oxidation in a platinum-containing monolith ($C_2H_6/O_2=1.2$, 1.2 atm, 20% N_2). The calculated outlet partial pressures are in very good agreement with the experimental values[1]. The profiles are obtained by simultaneously integrating heat and material balances along the monolith distance[1]. (In this figure, reaction time is used instead of distance because we wish to highlight how the ignition time relates to the residence time in the reactor). The calculations account for chemical reactions at the catalytic surface and in the surrounding gas phase. Except for the initial dissociative chemisorption of ethane, the kinetics of the elementary surface reactions are precisely those that are applicable in the partial oxidation of methane[11]. Accounting for axial dispersion did not affect the calculated profiles significantly and this is consistent with the observed good agreement between measured and calculated partial pressures and temperature at the reactor outlet when axial dispersion is ignored. The reactor operates nearly adiabatically; heat losses of about 25% were determined from the analysis[1]. Near the front of the reactor, oxygen and ethane are consumed exclusively at the catalyst surface producing H_2O, CO, and CO_2. The exothermicity of these reactions raises the temperature to a level at which the gas-phase reactions occur readily. The change in slope in the profiles of reactant partial pressures and temperature that appear at about 3.5 ms signals the onset of gas-phase ignition. This ignition time is consistent with the value shown in Figure 2 for a temperature of about 1123 K. After ignition, the reactions in the gas phase are largely responsible for the composition and temperature of the evolving mixture. Figure 3 compares calculated profiles for two of the gas-phase networks R_1 (Figure 3a) and R_3 (Figure 3b) discussed earlier. The purpose of this comparison is to emphasize that, in addition to ignition delay times, the kinetic trajectories predicted by the networks are also of importance. This figure shows that R_1 and R_3 lead to profiles that are very similar. However, some differences still remain. Network R_3, for example, predicts a higher degree of ethylene dehydrogenation to acetylene and hydrogen and the endothermicity of this reaction causes a corresponding decrease in temperature. These differences may warrant further investigation if the purpose of the analysis is to make a very accurate quantitative assessment of product distribution. Although not included here, it is noted that the reduced networks R_2 and R_4 lead to profiles that are nearly identical to those in Figures 3a and 3b, respectively.
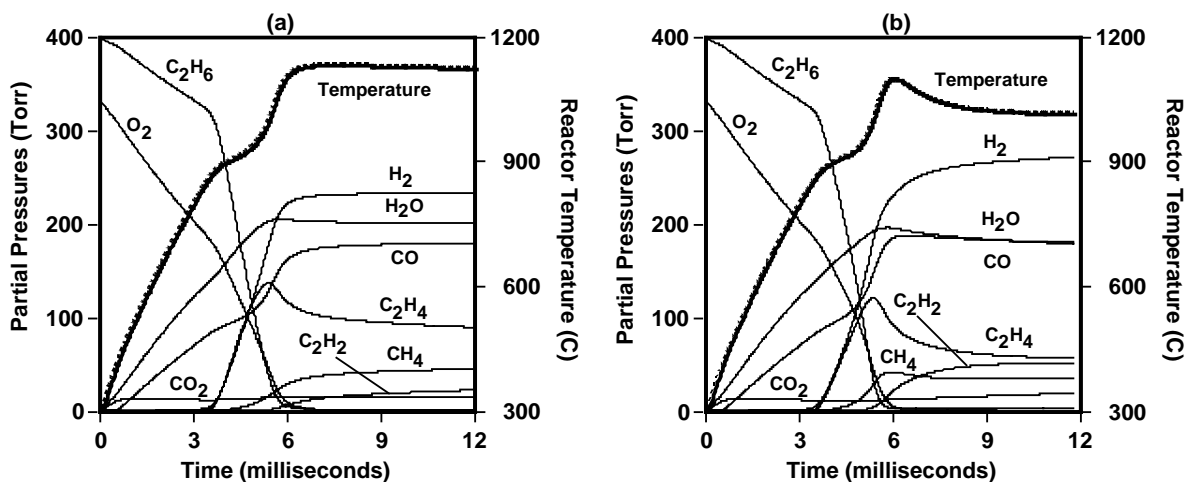
Figure 3. Partial pressures and temperature as a function of reaction time (a: network R_1; b: network R_3) [$C_2H_6/O_2=1.2$, 1.2 atm, 20% N_2 dilution, flow rate of 2 slpm, 5.88wt% Pt/α-Al$_2$O$_3$ monolith]

Figure 4 summarizes the salient result of the present analysis: the quantification of the relative contributions of the gas phase and catalytic reactions to the conversion process[1]. For the conditions of Figure 3a, this series of plots shows the region in the reactor where conversion in the gas phase and on the catalyst occurs. It also shows the extent of conversion occurring within these regions. The heat produced by the exothermic catalytic reactions in the front region of the monolith is clearly responsible for initiating gas-phase reactions that dominate the chemical transformations in the remainder of the monolith.
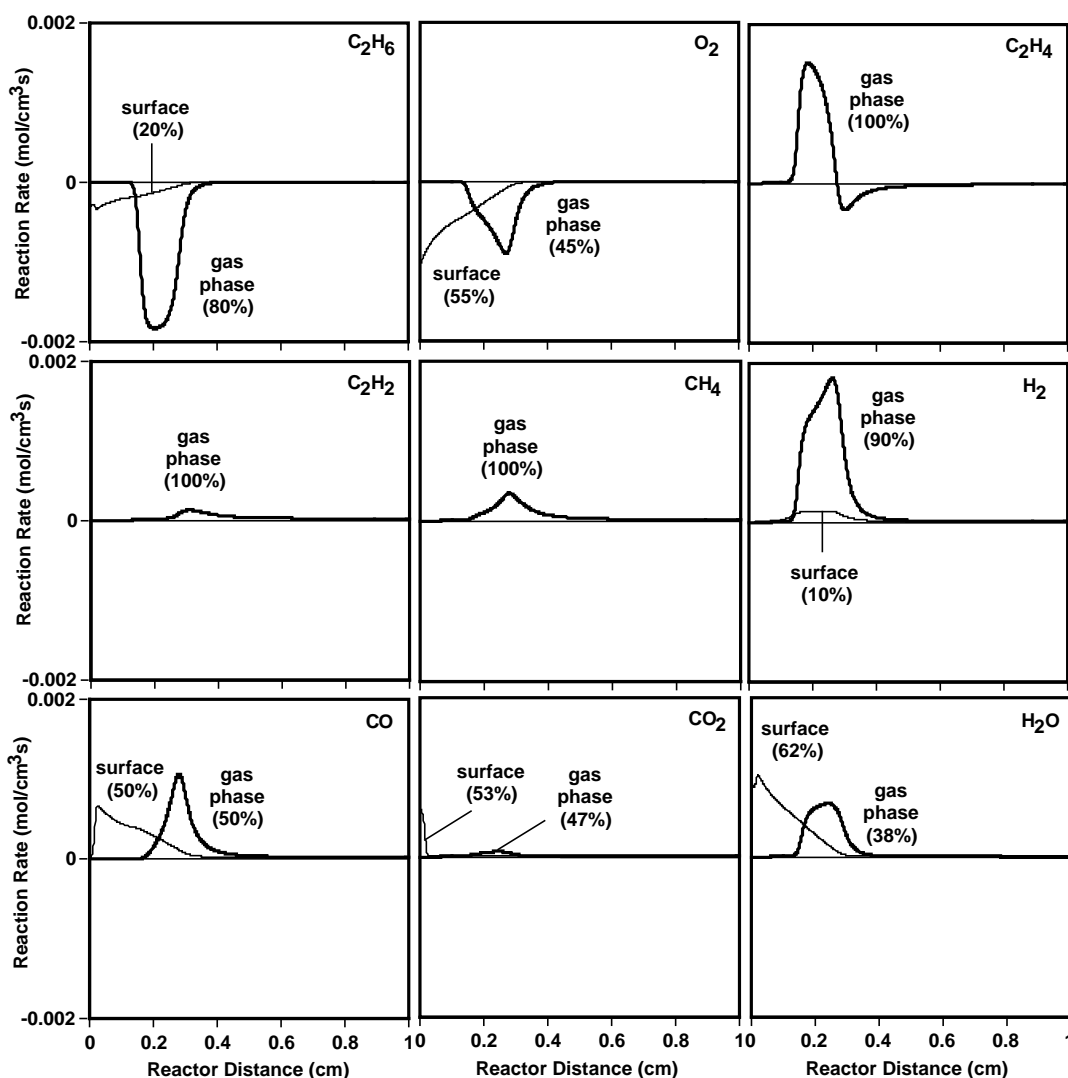
Figure 4. Reaction rates as a function of actual monolith distance. The curves are calculations for $C_2H_6/O_2=1.2$, 1.2 atm, 20% N_2 dilution, flow rate of 2 slpm, and a 5.88wt% Pt/α-Al_2O_3 monolith.

3. CONCLUSIONS

When ethane-oxygen mixtures rich in the hydrocarbon (C_2H_6/O_2 mole ratio = 1.2 to 1.8) are introduced at a temperature of 573 K to a platinum-containing monolith reactor, the conversion of the oxygen is complete and that of the ethane very high in reaction times in the vicinity of 10 ms. The reaction products, which include C_2H_4, C_2H_2, H_2, CO, H_2O, CO_2, and CH_4, do not correspond to thermodynamic equilibrium for such a reaction time, even when the ethane conversion is nearly 100%. The kinetics of the reactions, whether they occur on

the surface or in the gas phase, are therefore important in determining the product distribution.

Calculations using extensive kinetic information compiled by Schmidt and others for the surface reactions[11] have made it possible to calculate the rapid rise in temperature in the initial part of the reactor[1]. By the time the reaction gases have traversed roughly one-third of the reactor, the temperature is high enough for gas-phase reactions to occur readily. Ignition delay times calculated with reaction networks developed by various investigators[2,3] are well within the total residence time of the reactor. This finding strongly supports the conclusion that gas-phase reactions contribute significantly to the overall conversion of the ethane.

The determination of the axial temperature gradient and the ignition delay time for the gas-phase reactions are the most important factors in establishing the conclusion. Other issues of importance in the conversion of hydrocarbon-oxygen mixtures in general do not appear to play a significant role when the hydrocarbon is ethane. Such issues include interphase mass and heat transfer limitations, the adsorption and desorption of radicals from the surface, flame speed considerations involving back-diffusion of reactive intermediates, and other mechanistic features of gas-phase reactions that sometimes lead to negative temperature coefficients of reaction rates[3-8].

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