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Modeling of On-Line Catalyst Addition Effects in a Short Contact Time Reactor

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ABSTRACT

Recently developed short-contact-time reactors (SCTR), consisting of porous alumina monoliths coated with platinum, have been shown to produce ethylene from rich ethane/oxygen(/hydrogen) mixtures with yields and selectivities comparable to conventional steam cracking, using a reactor of much smaller size [1]. Although the overall mechanism is clearly autothermal and catalytic, the details, in particular the relative contributions of heterogeneous and homogeneous chemistry, are a matter of considerable debate. Recent experiments show that reactor performance can be further enhanced by dripping a dilute platinum solution onto the SCTR front face during reaction, resulting in catalyst deposition within only a short (several millimeter) zone of the reactor [2]. We have undertaken a computational study of this system, using two-dimensional computational fluid dynamics simulations with full heat and mass transport and detailed heterogeneous and homogeneous kinetic mechanisms. The results indicate that front-face catalyst loading enhances reactor performance by limiting the opportunity for heterogeneous ethane reactions that produce methane. As a result, ethylene selectivity increases and CH_4 selectivity decreases. The results strongly support a mechanism recently proposed by us, in which rapid, heterogeneous oxidation of adsorbed hydrogen consumes most of the oxygen [3]. The resulting heat is then released to the gas phase, causing homogeneous pyrolysis of ethane to occur in an environment containing much less oxygen. This mechanism explains not only the effects of on-line catalyst addition, but also the increase in ethylene selectivity observed upon addition of hydrogen to the reactant mixture.

INTRODUCTION

Ethylene production in the United States currently exceeds 55 billion lbs. annually, ranking it among the most important chemical commodities. Experimental development of so-called "short contact time reactors" (SCTR) by Schmidt et al. has lead to reactor configurations capable of remarkable ethane conversion and ethylene selectivity [1,4-8]. In these reactors, mixtures of ethane, oxygen, and nitrogen (with or without H_2) flow through a 1-cm-long reticulated foam ceramic monolith coated with a catalytic metal such as platinum. Autocatalytic operation is initiated by an external heat source applied temporarily. The reactor yields a mixture of ethylene, CO, H_2 , and H_2O , with smaller amounts of CO_2 , CH_4 , C_2H_2 , and higher hydrocarbons. The residence time in the reactor is typically less than 5 ms and reactor exit temperatures appear to be in the range 900 – 950 °C [1]. Ethane conversion and ethylene selectivity comparable to conventional steam-cracking technology can be achieved. Short-contact-time reactors are attractive because of their small size, high throughput, and near absence of coking, which commonly plagues conventional steam cracking reactors.

A new experimental configuration has been identified by Bodke and Schmidt [2] that consists of the addition of catalyst to an operating reactor, resulting in improved ethylene selectivity. This so-called "on-line" addition of catalyst involves the dripping of very small amounts of platinum salt, or other catalyst formulations, directly onto the front face of the hot reactor monolith. The resultant loading is less than 10% of that achieved using the conventional catalyst preparation technique, which results in a uniformly loaded catalyst. In addition to improved performance, this on-line process reduces the noble-metal requirement and permits rapid altering or regeneration of the catalyst.

In a recent paper, our simulations of SCTRs for ethane conversion to ethylene have indicated that both homogeneous and heterogeneous processes are important for the unique behavior of the SCTR system [3]. In this paper we use the same modeling methodology to study the on-line catalyst reactor configuration. Homogeneous and heterogeneous chemical-kinetic models are coupled to a full two-dimensional simulation of the fluid dynamics and heat transfer within a single

pore of an SCTR. We use the model to predict the production of various gas-phase species and calculate ethane conversion and product selectivities.

In this paper we focus on the simulation of the new experimental results in [2] in an attempt to explain the fundamental behavior of SCTRs, and to validate the chemical mechanisms presented in our previous work [3]. We find that the on-line addition of catalyst at very low loading produces a clear chemical effect related to the catalyst preparation technique. The front-face loading results in a catalyst coverage that persists over a distance shorter than the 1-cm length associated with uniformly loaded monoliths prepared in advance. Heterogeneous ethane decomposition is inhibited while the rapid oxidation of H_2 added to the inlet feed is not. Heterogeneous oxidation of either ethane or hydrogen is responsible for heat release that drives the endothermic dehydrogenation of ethane either in the gas phase or on the surface. Heterogeneous methane production is decreased in the on-line configuration, while the total production of ethylene is not. These findings are in general agreement with the conclusions drawn by Bodke and Schmidt [2]. In contrast to the conclusions in [2], we also find that an important contribution to the total ethylene production comes from homogeneous dehydrogenation of ethane. Previous reports have maintained that homogeneous processes are too slow to impact the product distribution in SCTRs [1], but our results indicate that both heterogeneous and homogeneous processes are important for ethane conversion in SCTRs.

Review of Experimental Investigations

There have been a wide variety of experimental investigations of the partial oxidation of ethane to ethylene over platinum-coated ceramic-foam monolithic supports in SCTRs. Of particular interest is the breakthrough work of Bodke et al. [1] performed prior to the consideration of on-line catalyst addition in SCTRs. In that paper, Pt and Pt-Sn alloy catalysts are used, and the addition of H_2 to the reactant feed mixture is reported for the first time. An ethylene selectivity of 85% with ethane conversion greater than 70% is obtained using C_2H_6 : H_2 : O_2 inlet mole ratios of 2: 2: 1 over a Pt-Sn catalyst. The authors conclude that the improved performance is a result of H_2 oxidation to

H₂O at the expense of ethane oxidation. This results in decreased selectivity to CO and CO₂. Heat released during this rapid hydrogen oxidation drives the conversion of ethane to ethylene with high selectivity. Three possible mechanisms to explain these observations are proposed [1]: (i) purely heterogeneous oxidation and dehydrogenation; (ii) purely homogeneous oxidation and dehydrogenation; and (iii) heterogeneous oxidation of hydrogen followed by homogeneous ethane dehydrogenation. A purely homogeneous model [9] is employed by the authors [1] in a non-flowing, transient analysis in order to address these mechanistic possibilities. The most promising scenario is heterogeneous hydrogen oxidation followed by oxygen-free homogeneous ethane dehydrogenation. However, the reported timescale (~10 ms) required to produce the measured conversion and selectivity by this process is far longer than that characteristic of the SCTR [1].

Because the focus of this paper is the simulation of the experimental on-line catalyst addition results in [2], we briefly summarize those results here. Monoliths prepared on-line have catalyst applied only over several millimeters, with ten times lower loading than monoliths prepared in advance, which have catalyst distributed over the entire length of the reactor (10 mm). Hydrogen added to a uniformly loaded Pt-catalyst reactor operating with a C₂H₆: H₂: O₂ feed ratio of 2: 3: 1 results in an ethylene selectivity of 72%, compared to 65% in the absence of added H₂. However, H₂ addition decreases the ethane conversion from 69% to 52% with a C₂H₆: H₂: O₂ feed ratio of 2: 3: 1. When the catalyst is added on-line to the front portion of the reactor, the ethylene selectivity increases to nearly 85% with C₂H₆: H₂: O₂ = 2: 3: 1, while the ethane conversion only decreases to 55%.

In the simulations reported here we show that the timescales for homogeneous dehydrogenation in a SCTR are indeed short enough to help explain the performance of these reactors. We present simulations that include detailed heterogeneous and homogeneous chemical-kinetic processes coupled to a two-dimensional flowfield model with full heat and mass transport. The results indicate that oxidation processes occur predominantly on the platinum surface, with only a minor oxidative contribution from the gas phase. In contrast, competitive pathways for ethane dehydrogenation and ethylene production occur in the gas phase. In addition, we show that

shortening the catalytic section of the reactor in the simulation results in decreased heterogeneous decomposition of ethane to form products such as CH_4 . Shortening of the reactor in the simulation is analogous to adding Pt catalyst on-line in an experimental reactor, where the Pt salt solution dripped onto the hot monolith face decomposes immediately and remains near the front of the reactor.

METHODS

Reactor Flow Modeling

The basic experiment to which we compare our simulations involves the reaction of ethane and oxygen with a nitrogen diluent and a hydrogen additive in a SCTR, shown schematically in Fig 1. Briefly, the experimental reactor consists of an α -alumina (92% Al_2O_3 , 8% SiO_2) monolith with 45 pores per inch (ppi) coated with a Pt loading of <0.1% by weight deposited on-line. The total mass-flow rate into the reactor is 5 slpm, with a reactor pressure of 1.2 atm. The nitrogen mole fraction is 30% when there is no hydrogen in the feed, and the ethane to oxygen mole fraction ratio is always 2:1. Error bars are not shown for the Bodke and Schmidt data [2], but it is stated that the product gas-phase carbon and hydrogen balances closed to within $\pm 5\%$.

In this paper we report simulations of the ethane SCTR using full heat and mass transport in a two-dimensional, axisymmetric flowfield. The fluid and heat transport are modeled using FLUENT [10], with a similar methodology to that used previously [3,11,12]. For this application, FLUENT solves the steady two-dimensional Navier-Stokes equations for laminar flow cast in a cylindrical coordinate system. Calculations performed on a Silicon Graphics Indigo II workstation required between 1 and 6 hours to converge, depending upon the solution initial guess.

The experimental reactor geometry along with the representation of a monolith pore used in the calculations is shown schematically in Figure 1 [12]. The axisymmetric-channel model serves as a reasonable geometrical simplification for a single continuously connected pore within the ceramic foam monolith. Experiments involving alternative support geometries indicate that the physical form of the support does not play a significant role in the reactor performance, and that straight

channel monoliths, although more difficult to work with, perform as well as foam monoliths [13]. In our simulations, the reactor monolith pore is 1 cm long and can have an active catalytic surface length ranging from 0-1 cm. The catalytic section is modeled as an α -alumina ceramic substrate having a monolayer coverage of platinum, resulting in a surface-site density of $\rho_s = 1.64 \times 10^{19}$ sites/m² (from the density of bulk platinum). Of the 1-cm length of the catalytic section of the reactor, only the first 2 mm is considered to be catalytically active in our current simulations. This corresponds approximately to the size of a drop of catalyst salt solution.

Chemistry Models

Using the standard chemical model within FLUENT [10], it is not possible to calculate the fractional coverages of surface species. This capability is necessary for incorporating a detailed heterogeneous reaction mechanism. For this reason we couple the main executable FLUENT code to external FORTRAN subroutines [12] that model the heterogeneous chemistry. Chemical reactions occurring on the surface consume some gas-phase species and produce others. In addition, heat may also be released or consumed as a result of these reactions. The net result of the external subroutines is to construct source terms consistent with the reactions occurring on the surface that are included in the conservation equations for each of the gas-phase species and for the enthalpy. A detailed discussion concerning the formulation of source terms and the determination of surface coverages can be found in [3].

For the gas-phase chemistry we use a methodology very similar to that used for the surface chemistry. A detailed kinetic mechanism is employed consisting of modified Arrhenius expressions, which can be subject to third-body collision enhancement factors, low-pressure treatments, and a Troe [14] bimolecular pressure fall-off treatment. The gas-phase-chemistry capability within FLUENT is more advanced than that for surface chemistry; however, it still lacks the flexibility to allow for low-pressure and fall-off treatments. Therefore, we again rely on external subroutines to interpret the gas-phase kinetic mechanism and develop the species and enthalpy source terms needed by FLUENT.

The detailed homogeneous and heterogeneous kinetic mechanisms are identical to those described in our earlier paper [3]. In summary, there are 25 reactive gas-phase species in the homogeneous mechanism, involved in 131 reversible reactions, with one additional irreversible reaction. This homogeneous mechanism is a subset of a much larger mechanism developed by Marinov, et al. [15] for the prediction of combustion behavior in rich CH_4 and ethane flames. Validation work involving comparison between simulations using this subset mechanism and additional experiments is the subject of another article currently in preparation. The heterogeneous mechanism consists of 20 surface species and 84 elementary reactions. Species containing more than two carbon atoms are not included in either the homogeneous or heterogeneous kinetic mechanisms, and there are no oxygenated hydrocarbons in the heterogeneous mechanism. Experiments measuring the selectivities to species with more than two carbon atoms indicate that the total selectivity to these species is approximately 5% across the entire range of H_2 inlet feed ratios [16]. In our simulations, the omission of these species leads to an over-prediction of the ethylene selectivity by approximately 5%. Oxygenated species are not found in experiments at the conditions considered here [1], but are found under leaner condition burning higher alkanes [17].

A schematic of the surface reaction pathways for the major carbon containing species is shown in Figure 2. Important features of this new heterogeneous kinetic mechanism include reversible ethane adsorption to form a surface ethane molecule. Ethane undergoes dehydrogenation to form surface ethyl directly, and by an oxygen-assisted route to form ethyl and hydroxyl. Ethyl undergoes further dehydrogenation to form ethylidene. Ethylene adsorbs reversibly into a π -bound ethylene configuration, and undergoes a reversible isomerization to ethylidene. The primary route leading to heterogeneous oxidation of carbon consists of ethylidene dehydrogenation to form ethylidyne. Ethylidyne then undergoes carbon-carbon bond scission to form methyl and surface carbon. Surface carbon oxidizes to form surface CO that can either desorb, or undergo further oxidation to form surface CO_2 . Surface methyl can recombine with an adsorbed hydrogen atom, resulting in CH_4 desorption. Surface hydrogen oxidizes to hydroxyl, which can then combine with another surface hydrogen to make H_2O , or disproportionate to form H_2O and O.

Despite the large number of reactions in the heterogeneous mechanism, there are relatively few adjustable parameters required to obtain agreement between the simulations and the experiments. Most values for kinetic parameters are either taken directly from previous work, or assigned nominal values which are not adjusted. A large portion of the surface carbon chemistry is taken directly from Wolf, et al. [18], in which simulations are compared to oxygen-free methane conversion to ethane experiments. The hydrogen oxidation subset is taken without modification from work we have performed which resulted in a mechanism explaining both ignition and steady-state oxidation at high temperature. That work is currently in preparation for publication. The values for the kinetic parameters used in that mechanism rely heavily on published values in the literature. Hydrogen and O₂ adsorption and desorption are from Rinnemo, et al. [19], H₂O desorption energy is from Fisher and Gland [20], radical species treatment is from Warnatz, et al. [21], and the surface oxidation reaction energetics are from Anton and Cadogan [22]. The carbon oxidation subset is very important for the current work, and the pre-exponential factors for surface carbon and CO oxidation, and CO desorption are adjustable parameters in the mechanism. The energetics for the carbon and CO oxidation reactions are taken from calculations by Shustorovich and Sellers [23], and experiments by Campbell, et al. [24]. The CO desorption energy is taken from further work by Campbell, et al. [25]. The other adjustable parameters are the pre-exponential factors for the recombination of ethylidene and hydrogen to form ethyl, and the dehydrogenation of ethylidene to form ethylidyne. These parameters influence the rate of heterogeneous hydrocarbon decomposition, and the production of CH₄ and CO through the subsequent ethylidyne carbon-carbon bond scission. Space limitations prohibit the tabular presentation of the chemical mechanisms developed and employed in this research. Electronic versions of these mechanisms can be obtained from the authors via e-mail.

RESULTS AND DISCUSSION

Simulation results are presented in Figs 3 and 4 and show that our combined homogeneous/heterogeneous mechanism can successfully reproduce both the trends and absolute

values of experimental data reported in [2]. The results in Fig 3a show selectivity to ethylene increases for all H_2 : O_2 mixture ratios when the catalyst is added on-line. This increase is small when there is no H_2 added to the feed, and becomes larger as the H_2 feed ratio increases. Taking into account that 5% selectivity to $>C_2$ species is observed in the experiments, and that this selectivity is implicitly included in our calculated ethylene selectivity, then the quantitative agreement is quite good as well. The predictions for the uniformly loaded catalyst are in excellent agreement with the measurements. The simulations of the on-line case tend to under-predict the experimental value at the highest H_2 feed by approximately 6% selectivity.

The results in Fig 3b indicate that adding catalyst on-line results in a decrease in CH_4 selectivity, which is consistent with the increase in ethylene selectivity shown in Fig 3a. Both the simulation results and the experiments [2] show that the decrease in CH_4 selectivity is more pronounced at the higher H_2 feed ratios. The agreement between the predictions and the experiments is again excellent when the catalyst is loaded uniformly. For the on-line case, the trend is predicted quite well, with the CH_4 selectivity increasing at a much lower rate than the uniformly loaded case as the H_2 feed ratio is increased. However, we tend to under-predict the CH_4 selectivity across the entire range of H_2 feed ratios by 1-2% selectivity.

The results indicate that ethane conversion in SCTRs is not greatly effected by the on-line addition of catalyst (Fig 3c). The experimental results [2] indicate that there is a decrease in conversion at the lower H_2 feed ratios when the catalyst is added on-line, but that at the higher H_2 feeds there is a slight increase. The simulations capture this behavior quite well at the lower H_2 feeds, but do not predict the cross-over observed at the higher feeds. Neither the physical mechanism(s) responsible for the cross-over observed experimentally, nor the reason(s) for the simulations not capturing this behavior are well understood at this time. Nevertheless, the largest discrepancy between the predicted and measured results is only 9% conversion, or approximately 15% relative error.

While the results in Fig 3 strongly suggest that the effect of on-line catalyst loading is to reduce the opportunity for deleterious (i.e., methane-producing) heterogeneous reactions to occur by

minimizing the amount of catalyst in the reactor, a comparison of the predicted gas-phase and surface rates of production confirms this supposition. In Fig 4 we show the calculated total molar rates of homogeneous and heterogeneous consumption or production of three important gas phase species. Ethane consumption rates are displayed in Fig 4a, which show heterogeneous consumption is larger (more negative) than homogeneous consumption for all H_2 feed ratios, but that competition between the processes is close. The ratio of heterogeneous to homogeneous consumption rates is 8.5 without H_2 in the feed, and drops to ratios near unity at the highest H_2 feed ratios. The results in 5a also indicate that on-line catalyst addition on the front face of the reactor causes a larger fraction of the ethane to be consumed homogeneously, and at the expense of the heterogeneous process. The shorter catalytically active section associated with the on-line configuration inhibits heterogeneous decomposition of ethane, and this permits homogeneous processes to compete more effectively for the available ethane. Hydrogen-atom attack on ethane to produce C_2H_5 and H_2 and the decomposition of C_2H_5 to form ethylene and H are the most important homogeneous reactions. The rates of these reactions are strongly influenced by temperature, and the simulations show that the peak temperature near the front of the reactor is 30 K higher for the on-line case than for the uniformly loaded case. This is due in part to the lack of endothermic hydrocarbon-cracking surface reactions in the downstream portion of the reactor in the on-line configuration.

The results shown in Fig 4b indicate that enhanced homogeneous decomposition of ethane results in a greater homogeneous production rate of ethylene. While the heterogeneous production rate of ethylene is larger than the homogeneous rate for nearly all conditions studied, the on-line configuration results in a larger fraction of the production to occur in the gas phase for all H_2 feed ratios. The total rate for ethylene production is slightly lower for the on-line configuration, yet the selectivity is seen to increase. This is because the production of CH_4 is decreased, as we discuss next. In addition, ethane conversion has also decreased, and product selectivity is based only on the amount of reactant converted.

In Fig 4c we compare calculated homogeneous and heterogeneous CH_4 production rates for both catalyst preparation methods. Of particular interest is that homogeneous production of methane is always small, and not strongly affected by the preparation method. Conversely, on-line preparation causes a substantial decrease in heterogeneous CH_4 production compared with uniformly coated monoliths. Thus the total rate of CH_4 production is sharply decreased due to on-line preparation and the associated lack of catalyst length over which to crack C_2 hydrocarbons to methane. This occurs to the extent that decreased selectivity results despite the slightly smaller amount of ethane converted.

CONCLUSIONS

Our simulations indicate that the fundamental behavior of the ethane SCTR prepared with catalyst added on-line is the result of coupled heterogeneous and homogeneous chemical processes. It seems clear that low CH_4 selectivity results from the lack of heterogeneous CH_4 production downstream in SCTR's prepared with the catalyst added on-line to the front portion of the monolith. Total ethane consumption and ethylene production rates are less strongly affected because the homogeneous route for these processes compensates for the loss of heterogeneous activity, whereas the production of methane is much more effective as a heterogeneous process. Because the ethane conversion remains high, a decrease in CH_4 selectivity is accompanied by an increase in the ethylene selectivity. These results indicate that the improved performance observed as a result of on-line catalyst addition is not due to decreased ethylene decomposition, but is because heterogeneous ethane decomposition is inhibited. If only the heterogeneous process were in effect, then the observed decrease in heterogeneous methane production would have to be the result of a decrease in heterogeneous ethylene decomposition. This would result in an increase in heterogeneous ethylene production, which is not what our predictions indicate. We show a decrease in heterogeneous ethylene production compensated for by an increase in homogeneous production. The fundamental chemical processes that drive the performance of ethane SCTR's can

be summarized as heterogeneous oxidation occurring near the front of the reactor, coupled via heat transport to homogeneous dehydrogenation of ethane to produce ethylene and H_2 .

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CAPTIONS

- Figure 1 Schematics of the experimental SCTR showing the heat shield and central catalytic section (top), and the single-pore reactor model (bottom). A front heat shield is not in place during experiments with on-line catalyst addition.
- Figure 2 Schematic representation of the important surface reaction pathways for carbon containing species. Adsorption/desorption processes are also indicated.
- Figure 3 Comparison between predicted and experimental selectivities and conversion as a function of $H_2:O_2$ for $C_2H_6:O_2 = 2.0$. (a): Ethylene selectivity (b): Methane selectivity (c): Ethane conversion. Closed symbols indicate experimental data, open connected symbols indicate simulation results. Circles indicate catalyst loaded uniformly, squares indicate on-line catalyst addition.
- Figure 4 Calculated total molar reaction rate for homogeneous (closed symbols) and heterogeneous (open symbols) processes. Uniformly coated monolith results are shown connected by dashed lines, and on-line results are shown connected by solid lines. (a): Ethane, (b): ethylene, (c): methane.

Figure 1

Figure 2

Figure 3

Figure 4