COMBUSTION INITIATION BY PALLADIUM CATALYSTS

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Summary The use of heterogeneous systems to initiate combustion has widespread application such as the use of nano-catalysts for high performance propulsion applications. The current work investigates the conversion of fuel rich ethane mixtures, flowing over an alumina supported porous media based palladium (Pd) catalyst, to more reactive blends in order to understand the partial combustion process. The heterogeneous chemistry was developed using a semi-automatic mechanism generation method featuring four reaction classes (direct adsorption, adsorption onto a pre-existing adsorbate, surface reactions and unimolecular reactions) in order to produce a comprehensive reaction mechanism featuring 285 reversible reaction steps for 34 adsorbates. The model was coupled to a gas phase reaction model featuring 271 reversible reaction steps and 44 species and validated by comparisons with experimental data obtained in a cylindrical micro-reactor by Ineos Technology Ltd. The sensitivity to important physical and chemical parameters was investigated in order to establish their influence on predictions.

BACKGROUND

The development of a heterogeneous chemical kinetic mechanism for reacting flows of hydrocarbons over an alumina supported Pd catalyst is outlined with validation performed for the initiation of combustion reactions in fuel rich mixtures. The applied mechanism was constructed using the methods developed by Vincent et al. [1] and incorporated into an axi-symmetric, two-dimensional boundary layer solver in order to model a representative virtual pore passing through a catalytic bed. The computations couple a thoroughly validated homogeneous gas phase chemical kinetic model with a heterogeneous mechanism constructed on the basis of four reaction classes: direct adsorption, adsorption onto a pre-existing adsorbate, surface reactions and unimolecular reactions. The heats of adsorption for the surface species in the base case catalytic model were obtained with the non-geometrical UBI-QEP method of Shustorovich and co-workers [2]. The method was applied in a consistent manner with results from *ab initio* and experimental investigations used for the determination of the heats of adsorption [1, 2]. The atomic heats of adsorption (Q_{0A}) for the three elements (H, O and C) considered here are of fundamental importance. The values for Q_{0H} (155.6 kJ/mol) and Q_{0O} (218.8 kJ/mol) correspond to experimental values. However, Q_{0C} (401.7 kJ/mol) was obtained indirectly and subject to large uncertainties as discussed below. The derived heat of adsorption of OH is also subject to uncertainties with Vincent et al. [3] selecting a Density Functional Theory (DFT) derived value in a study of the corresponding platinum (Pt) system. Lv et al. [4] studied Pd surfaces using DFT and suggested a value for $Q_{OH(s)}$) of 236 kJ/mol with Hansen and Neurock [5] recommending 209 kJ/mol. Patrito et al. [6] established a dependency of $Q_{OH(s)}$ on surface coverage effects and it was observed that at low oxygen coverages the adsorption of hydroxyl is strongly influenced by any existing OH coverage leading to the formation of a non-uniform distribution. In such cases, the heat of adsorption of OH is favoured by the possibility of establishing hydrogen bonds. Such effects have been accounted for here. The developed models were validated by comparing with experimental data obtained for the catalytic partial oxidation of ethane through a 1%Pd/Al_2O_3 foam bed placed in a cylindrical quartz microreactor. The catalyst was prepared by impregnation of a lithium aluminium silicate (LAS) support, washcoated with high purity alumina (HPA). Pre-treatment by calcination was carried out at 1473 K in air for 6 hours. The catalytic bed, a 30 mm section of HPA washcoated LAS foam of 28 mm diameter, was followed by a 197 mm inert section with a pore density of 30 pores per inch foam and a porosity of 80 %.

RESULTS AND DISCUSSION

The analysis of fundamental physical properties resulted in the selection of a set of model parameters applied in the construction of the preliminary base case mechanism used in a parametric sensitivity analysis. Examples of results obtained with the basic model can be seen in Fig. 1 for different oxygen to carbon weight ($0.3 < O/C < 0.8$) ratios and a constant molar hydrogen to oxygen ($H_2/O_2 = 2$) ratio. Overall, the model reproduces trends in conversions and selectivities in an adequate manner. The temperature appears underpredicted, though measurements are particularly difficult in the current configuration and the product distribution as a function of conversion is a more reliable measure of accuracy. The selectivity to CO is also reproduced fairly well. However, the carbon selectivities to C_2H_4 and CH_4 are significantly in error and corrections are evidently required. The ratio is critical in combustion applications due to the different reactivities of the species. A systematic variation of physical parameters provided useful insight into the sensitivities of the system though no combination of variations was found to adequately correct the imbalance. In particular, the modifications failed to address the the chemical patterns that lead to a preferential selectivity towards C_1 species, especially methane, in the initial stages of fuel conversion. Hence, the critical role of the catalytic chemistry must to be assessed in terms of fundamental parameters used in the model construction for the heterogeneous chemistry over Pd. In particular, the observation that C-C bond scissions occurs at an early stage is in contrast to mechanistic studies featuring similar systems [7, 8, 9].

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Shustorovich et al. [10] used trends in heats of adsorptions upon metals to determine a value for Q_{0C} on Pd with the result subsequently applied fairly consistently in studies that adopt the UBI-QEP formalism. However, it appears that the estimation is not sufficiently accurate for the current purposes and a sensitivity analysis was performed as outlined below.

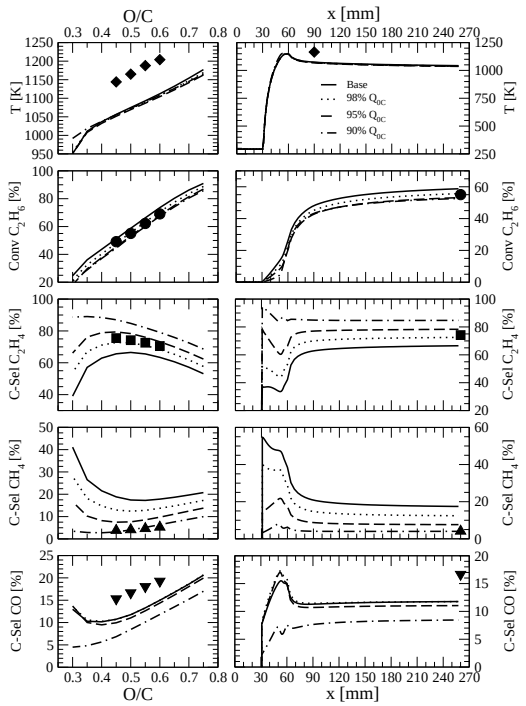

Figure 1. Temperatures, conversions and selectivities of key species across the O/C range (left) and the axial evolution at O/C = 0.5 (right) for a variation in Q_{0C}.

Bradford [11] reported the fundamental importance of $Q_{C(s_3)}$ for modelling catalyst behaviour and quotes a value for adsorption on Pd/SiO_2 that is reduced by $\sim$18%. Paul and Sautet [12] presented results obtained with two different DFT methods and Neurock and Van Santen [13] performed small cluster and periodic slab DFT calculations of $Q_{C(s_3)}$ adsorption on Pd(111). Chen et al. [14] also provided DFT slab calculations for $Q_{C(s_3)}$. Discrepancies compared to the suggestion by Paul and Sautet [12] were attributed to differences in the slab thickness. Neyman et al. [15] reported an extensive study of the adsorption of carbon on Pd clusters. The computations featured large clusters. Given the above uncertainties, a sensitivity analysis was performed using an envelope chosen to cover the principal spectrum, with Q_{0C} reduced by 2%, 5% and 10%. The results are presented in Fig. 1. It is evident that a reduction in this fundamental parameter is beneficial with the C_1/C_2 balance gradually corrected. The carbon selectivity to CO suffers a modest adverse effect if Q_{0C} is decreased by more than 5%. A 10% reduction greatly modifies the initial C_1/C_2 balance in favour of the latter and matches the selectivity to methane most accurately. However, the overall reduction in adsorption energies is such that there are less hydrogenated species adsorbing and, as a consequence, lower levels of H(s) from dehydrogenation reactions. This leads to a reduced presence of OH(s), which is the main oxidative agent of $C(s_3)$, and to reduced production of CO via $CO(s_2)$ desorption. A 5% reduction in the heat of adsorption of carbon produces an adequate C_1/C_2 balance whilst maintaining CO levels. Thus, the value suggested by Neyman et al. [15] (Q_{0C} = 381 kJ/mol), which coincides with a 5% reduction in carbon adsorption energy, was chosen to produce the final mechanism.

CONCLUSIONS

A heterogeneous mechanism for the simulation of ethane conversion over palladium catalysts has been developed and the sensitivity to key physical and chemical parameters investigated. It has been shown that the influence of the catalytic chemistry determines the final product distribution. In particular, the impact of the atomic heat of adsorption of carbon on Pd was investigated and it was concluded that, in line with more accurate DFT studies, a decrease in the value by 5% has a positive impact on the predictive accuracy of the model. Comparisons with experimental data shows that parameters such as the CH_4/C_2H_4 ratio, critical in combustion applications, can be reproduced as a function of fuel conversion.

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