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Interactions between heterogeneous and homogenous chemistries: hierarchy of reactor models for the Catalytic Partial Oxidation of hydrocarbons

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Highlights

- Honeycomb reactor for partial catalytic oxidation
- CFD simulation of monolithic reactors with detailed kinetic models
- Interactions between homogeneous and heterogeneous chemistry

1. Introduction

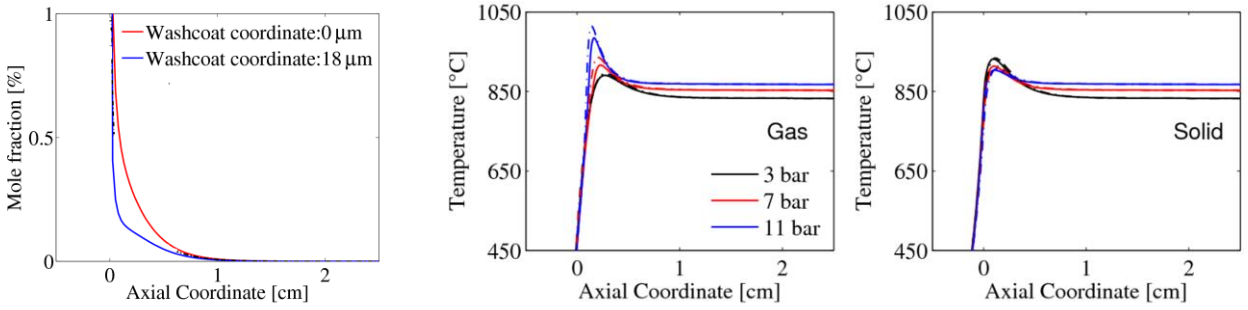
The interactions between surface and gas-phase chemistries is a crucial issue for high-temperature catalytic processes. The physical and chemical phenomena, which occur in the gas-phase and on the catalyst surface, strongly influence the conversion and selectivity to the desired product of the process. In this regard, an assessment of the main homogeneous and heterogenous routes along with their synergy is essential for an optimal design and safe operation of the reactor. This becomes particularly true for the ultra-fast conversion of hydrocarbons in short-contact-time reactors, playing a key role in the worldwide growing demand of alternative sources of energy. One important example of such applications is the catalytic partial oxidation (CPO) of the hydrocarbons to syngas. This process is carried out in auto-thermal and compact reactors, with noble metal catalysts. They are characterized by high exothermic and endothermic reactions, which create sharp gradients of temperature and concentration within the small reactor volumes, promoting the gas-phase kinetics. In this context, the coupling and the interactions between homogeneous and heterogenous chemistry strongly influence the overall performances of the reactor. This requires a detailed model of the reactor able to accurately account for all the aspects involved in gas-phase, surface chemistries and transport phenomena. In this work, we develop a a multiregion Computational Fluid Dynamics (CFD) model able to account for all these levels of detail [1]. In view of the high computational cost, we present also an assessment of lower hierarchy models (e.g., 1D heterogeneous model) in order to validate and assess their adequacy in modeling the synergy between homogeneous and heterogeneous chemistries.

2. Methods

We considered as case study the CPO of propane over rhodium in auto-thermal honeycomb reactors [2]. The fundamental analysis is carried out using the *catalyticFoam* solver [1], which enables the CFD description of the gas phase by accurately solving the Navier-Stokes equations. The framework account for the diffusion and reaction within the washcoat by describing the catalyst as a pseudo-homogeneous phase with effective transport properties and solving the transport equations for species and temperatures. The gas-phase and heterogeneous chemistries are described by means of microkinetic models. The results of the CFD model are interpreted by means of the cup-mix average in the gas-phase and through area-weighted average in the washcoat. The simplified model employed is a 1D heterogenous model consisting of mass and energy balances for the gas and solid phases, as well as a site balance for the adsorbed species. The description of the surface chemistry is implemented in the models by using a single site C_1 micro-kinetic scheme over Rh [3]. This micro-kinetic scheme is extended to C_3H_8 by adding two lumped steps for the activation of propane [2]. The gas-phase chemistry of C_1-C_3 species is described through a detailed kinetic mechanism [4]. The simulations are carried out in adiabatic conditions representative of the working conditions of these reactors.

3. Results and discussion

We first investigated CPO of propane on Rh with the detail multiregion CFD model, accounting both for the contribution of the gas-phase chemistry and of the spatially-resolved heterogeneous reactivity in the catalytic washcoat. The results of the detailed model show that the oxygen consumption is under fully external mass transfer limitations, as already reported in literature [2]. On the contrary, the fuel (i.e, propane) develops a concentration gradient within the washcoat as depicted in Figure 1(a). Negligible variations of the gradient intensity are observed by changing the pressure and, ultimately, the intensity of the homogeneous chemistry. The analysis of the temperature profile is presented in terms of axial profiles in the gas and solid phase in Figure 1(b). An increase of the pressure leads to an opposite behavior for the temperature in the gas and in the washcoat. On the solid side, a pressure increment results in a decrease of the catalyst temperature. On the contrary, the gas temperature increases and the hot-spot becomes more pronounced especially at higher pressure. At low pressure, the contribution of the gas-phase chemistry turns out to be negligible and the reactivity of the system is mainly controlled by the heterogeneous reactions. In these conditions, the temperature of the catalyst is higher than the temperature of the gas phase. As the pressure increases, the intensity of the homogeneous chemistry is enhanced and the temperature in the gas phase overcomes the temperature of the solid phase. This results in an inversion between the temperature profiles, as shown in Figure 1(b) [2]. The 1D model well describe the reactor when the influence of the homogeneous chemistry is negligible as occurs at low pressure. By an increase of pressure, deviations between CFD and 1D starts to develop as a result of the complex radial temperature and concentration gradients promoted by the presence of the gas-phase chemistry.



(a) (b)

Figure 1. Concentration of propane in the washcoat at two different thickness along the reactor (a); temperature profile in the gas ans solid phase at different pressures (b) – CFD: solid line – 1D: dashed line

4. Conclusions

The CFD simulations provided a detailed insight in the complex phenomena characterizing the strong coupling between heterogeneous and homogenous chemistries in the catalytic partial oxidation of propane on Rh. The results are in line with experimental observation previously reported. Simplified lumped models have been assessed and are found to be able to describe the behavior of the reactor when the contribution of the homogeneous chemistry is negligible, whereas deviations start to develop at high pressure when the gas phase chemistry is important.

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Keywords

homogeneous chemistry; heterogeneous chemistry; CFD; catalytic partial oxidation