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# Two-dimensional detailed modeling of fuel-rich $H_2$ combustion over $Rh/Al_2O_3$ catalyst

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## Abstract

The previous analysis of experiments of $H_2$ fuel-rich combustion over a Rh catalyst—reported in Maestri et al. [2007. Role of gas-phase chemistry in the rich combustion of $H_2$ and CO over a $Rh/Al_2O_3$ catalyst in annular reactor. Chemical Engineering Science 62, 4992–4997]—has been extended using a detailed surface kinetic model coupled with a detailed kinetic scheme for $H_2$ gas-phase combustion. The model is now able to investigate possible interactions between the surface and homogeneous chemistries. Results suggest that the homogeneous chemistry played a role, especially at high temperatures. In the intermediate range of temperatures, where the experimental conversion data are systematically higher than those corresponding to the diffusive limit, model predictions revealed that a very weak interaction between the gas-phase and surface kinetics occurs. In fact, the fraction of radicals that desorbs from the surface is significantly lower than that needed in order to partially activate the homogeneous process. Finally, we accounted for the presence of zones upstream and downstream of the main catalytic bed with a low catalytic activity. These sections could be related to non-uniformity of the catalytic washcoat at the boundaries of the catalytic bed, uncertainty of the beginning and ending of the washcoat layer, and possible evaporation and redeposition of the catalyst. We show that such low activity sections could significantly increase the conversion above the diffusive limit and provide a plausible mechanism to rationalize the experimental data. Moreover, dynamic simulations further revealed that under isothermal conditions the ignition of the homogenous process is governed by a build-up of a "radical pool" at the reactor back end followed by upstream propagation: axial diffusivity is crucial in order to model appropriately the experimental data.

*Keywords:* Catalytic partial oxidation; Heterogeneous–homogeneous detailed kinetics; Annular reactor; 2D reactor modeling; Fuel-rich catalytic combustion; Hydrogen; Rhodium; Rh evaporation and redeposition; Dynamics

## 1. Introduction

The possible interaction between heterogeneous and homogeneous reactions represents an important issue for high temperature catalytic processes. This is the case also of short contact time processes in the catalytic conversion of hydrocarbons to chemicals (synthesis gas, olefins or oxygenates), which have been extensively explored during the last 15 years, following up the pioneering work of Schmidt's group (Hickman and Schmidt, 1992, 1993; Huff and Schmidt, 1993, 1994).

In the case of methane the literature suggests, based on results of experimental and theoretical investigations, that the partial oxidation to synthesis gas is mainly due to the heterogeneous chemistry, while gas-phase reactions are expected to play a role only at high pressures (Deutschmann and Schmidt, 1998; Davis and Schmidt, 1999; Goralski et al., 2000; Appel et al., 2005; Mhadeshwar and Vlachos, 2005; Quiceno et al., 2006; Eriksson et al., 2007). It must be considered that most of the methane partial oxidation tests reported and modeled in the literature are characterized by complete conversion of oxygen,

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the limiting reactant, within a small reactor length, and, due to the subsequent prevailing role of endothermic reactions, a progressive decrease of temperatures downstream along the monolith channels. However, in previous work (Maestri et al., 2005), we showed, through dynamic simulation of autothermal reactors with different support geometries (honeycombs vs. foams vs. small spheres), that for high flow rates, the oxygen conversion can be incomplete. Thus, conditions that could favor the homogeneous process (high temperatures, unconverted oxygen co-existing with synthesis gas) can occur within microchannels.

Several examples are reported in the experimental and theoretical literatures that indicate the possible interplay between the heterogeneous and homogenous chemistries in $H_2$ combustion (Norton et al., 2004). Vlachos modeled the coupled homogeneous–heterogeneous oxidation of hydrogen over a platinum surface in a stagnation point flow reactor (Vlachos, 1996). He found that the presence of a catalytic wall partially inhibited the homogeneous process. Chattopadhyay and Veser (2006) presented a 2D plug-flow model of a microchannel reactor with detailed kinetics both for the surface and the gas-phase.

In our previous work (Maestri et al., 2007), we presented short contact time experiments of rich combustion of $H_2$ and CO in an isothermal annular reactor, under mass transfer limited consumption of $O_2$. Quantitative analysis of the experimental results was conducted via a 2D model of the annular reactor, that coupled molecular kinetics for the catalytic oxidations of CO and $H_2$ describing the overall surface reactions (Tavazzi et al., 2006) to the detailed kinetic scheme of Ranzi and co-workers for the gas-phase (Frassoldati et al., 2006). Interestingly, conversions higher than the mass transfer limit were experimentally measured, and this "puzzle" remains unexplained (we refer below to this phenomenon as a '*conversion enhancement*'). In line with the experimental data, the theoretical analysis pointed out that gas-phase reactions start playing an important role only in the case of the $H_2/O_2$ reacting system at temperatures close to or above 650 °C, at which the homogeneous process overtook the catalytic one and yielded complete conversion of $O_2$. Radical seeding simulations were then performed to verify whether at temperatures lower than 650 °C interactions between heterogeneous and homogeneous reactions could be envisaged. Those simulations pointed out that partial activation of the homogeneous process was possible with inlet radical mole fractions higher than $10^{-6}$. Given the lumped nature of the heterogeneous kinetics, we could not verify whether those radical mole fractions were compatible with desorption of intermediates from the catalyst surface and thus responsible for the enhanced reactivity over the mass transfer limit. This motivates the present work.

In this work, the previous mathematical treatment of the annular reactor was extended by incorporating a detailed kinetic scheme of the $H_2/O_2$ reacting system on Rh catalysts (Mhadeshwar and Vlachos, 2005; Maestri et al., 2008). This improved model was employed to analyze the $H_2$-rich combustion experiments in the annular reactor and investigate possible interactions between catalytic and gas-phase reactions. Moreover, herein a detailed description of the 2D model of the annular reactor is presented and details are given on the numerical strategy adopted to address the complexity of a process with strong radial and axial gradients (a common feature of short contact time partial oxidations in microchannel reactors).

## 2. Experimental

In previous work (Tavazzi et al., 2006), catalytic tests of $H_2$ combustion were performed as a part of a kinetic investigation on the production of $CO/H_2$ mixtures via partial oxidation of $CH_4$ over a supported Rh catalyst. Namely, the kinetic study was carried out over a 0.5% (wt/wt) $Rh/\alpha\text{-}Al_2O_3$ catalyst, prepared by grafting of alumina powders with $Rh_4(CO)_{12}$.

Catalytic tests were performed in an annular duct reactor, wherein a uniform and well adherent catalytic layer (1.5 cm long, 40–50 μm thick) was deposited according to an optimized procedure over the external surface of a mullite tube that was coaxially inserted into an outer quartz tube giving rise to an annular duct through which the gas mixtures flowed in the laminar regime; the inner diameter of the quartz tube measured 9 mm and the aspect ratio of the annular duct (that is the ratio between inner and outer radii of the concentric annular section) amounted to 0.528 (Tavazzi et al., 2006). The catalyst loading was on the order of 10 mg. The inner cavity of the mullite tube also served as a channel for a sliding K-type thermocouple by which the axial temperature profiles of the catalyst were measured. The correspondence of the measurements to the actual temperatures on the catalyst surface was ensured by the thermal equilibrium across the section of the ceramic tube, due to the negligible contribution of the thermal dispersion along the mullite tube on the overall heat dissipation (Ibashi et al., 2003). Upstream the catalytic bed, an inert bed ($\sim$ 30 cm) was also present and the experimental rig (inert and catalytic bed) was positioned inside a tubular furnace. Before entering the catalytic bed, gas stream, flowing through the inert section, equilibrated the oven temperature, practically reproducing a preheated feed situation. The effective dissipation of the reaction heat by radiation from the catalyst surface to the oven inner wall helped realizing catalytic tests at the expense of acceptable thermal axial gradients (mostly below 5 K/cm), when compared with those obtained in packed-bed reactors. Experiments of $H_2$ combustion were performed under rich conditions ($H_2/O_2/N_2 = 4/1/95\%$, v/v), in order to recreate conditions similar to those in the partial oxidation of $CH_4$.

## 3. Mathematical model

### 3.1. Assumptions and governing equations

A dynamic, isothermal, isobaric, 2D model of a catalytic annular reactor was developed. A sketch of the annular reactor is reported in Fig. 1.