CATALYTIC METHANE COMBUSTION ON A PLATINUM-GAUZE: EXPERIMENTAL REACTOR PROFILES, SPATIALLY RESOLVED LASER INDUCED FLUORESCENCE SPECTROSCOPY AND NUMERICAL REACTOR SIMULATIONS

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Abstract

In the present contribution concentration profiles around a single Pt-gauze are resolved experimentally for the catalytic combustion of methane \( \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \). Stable molecules are measured by a capillary sampling technique. OH\(^{•}\) radicals are detected and quantified by fiber-based laser induced fluorescence spectroscopy. The experimental profiles are compared with numerical reactor simulations including the 3D structure of the gauze, detailed surface chemistry, detailed gas phase chemistry and mass and heat transport. Both, experiment and simulation, confirm pronounced mass and heat transport limitations. Full CH\(_4\) conversion is observed experimentally, even though the gauze wires are only 40\(\mu\)m in diameter and 127 \(\mu\)m apart. Simulations with and without gas phase chemistry show that surface reactions alone cannot account for full conversion. About 25% conversion can be attributed to gas phase reactions, which are linked to the catalytic reactions via exchange of species, heat and radicals.

Keywords
catalytic gauze, methane combustion, concentration profiles, OH\(^{•}\) radicals, LIF, simulation

Introduction

Reactions on catalytic gauzes are among the oldest processes in the chemical industry. Gauze catalysts are used for highly exothermic and extremely rapid reactions like ammonia oxidation (Ostwald process) or the ammoxidation of methane and ammonia to hydrogen cyanide (Andrussow process). Catalytic gauze reactors operate adiabatically and reactor performance is dictated by mass and heat transport. Little is known about the intrinsic kinetics of the catalytic reactions and the role of gas phase chemistry. In the present contribution the steep concentration gradients in the boundary layer of the gauze are resolved for the catalytic combustion of methane as model reaction.

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H^\circ = -803 \text{ kJ/mol} \quad (1) \]

Stable molecules are measured by a capillary sampling technique. OH\(^{•}\) radicals, an indicator of gas phase reactions, are detected and quantified by fiber-based laser induced fluorescence spectroscopy. The experimental profiles are compared with numerical reactor simulations including the 3D structure of the gauze, detailed surface chemistry, detailed gas phase chemistry and mass and heat transport.

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Reactor Profile Measurements

Fig. 1 Experimental setup.

Fig. 1 shows a schematic of the experimental setup. The platinum gauze consisted of 3600 meshes/cm² with a wire diameter of 40 μm and was clamped inside a heated fused silica reactor operated at an absolute pressure of 1.5 bar. The sampling capillary could be traversed along the center of the reactor with micrometer precision allowing reactant mixture samples to be extracted continuously with high spatial resolution. The spatial resolution was verified using CFD simulation of the sampling process. The furnace was set to 700°C. The feed flowed from bottom to top and consisted of 120 ml·min⁻¹ CH₄, 480 ml·min⁻¹ O₂ and 2400 ml·min⁻¹ Ar as diluent and internal standard.

Laser Induced Fluorescence Spectroscopy (LIF)

OH• radicals were detected and quantified by LIF using an excitation of the OH• A→Σ - X→Π 0→1 band head at 281nm while detecting the 1→0 and 1→1 bands (306-330nm). The spatial resolution of the fiber probe was determined by geometric considerations and the effects of spatial averaging were removed by deconvolution. LIF was also used to determine the inlet temperature of the computational domain from an excitation scan 4mm downstream the gauze and analysis of the rotational line intensities (Boltzmann plot).

Numerical Simulations

Numerical simulations were conducted in STARCCM+ Vers. 10.04 (finite volume method) on a linux cluster. The 3D structure of the gauze was considered by modeling ¼ of a mesh from 2mm upstream to 2mm downstream the gauze. The Navier-Stokes equations were solved together with equations for species and energy conservation. Velocity, temperature and species mass fractions were specified at the inlet. A pressure outlet boundary condition was used at the outlet. Periodic boundary conditions were specified for all other boundaries. Temperature and composition dependence of viscosity and thermal conductivity was considered according to kinetic theory of gases. Specific heats were calculated from NASA polynomials. Mass averaged molecular diffusivities were calculated from binary diffusivities. The surface mechanism for methane oxidation on Pt was taken from Deutschmann et al. (1996). The GRI 3.0 mechanism was used to describe methane combustion in the gas phase (Smith et al., 1999).

Results and Discussion

Figure 2 shows the measured and simulated profiles for the main species and the calculated temperature (top) and the minor species, and OH• radicals (bottom).

Diffusion causes CH₄ and O₂ to decline from -1.5mm on as well as detection of CO₂ and H₂O in front of the gauze. Full CH₄ conversion is observed experimentally. Simulations with gas phase chemistry (solid lines) and without (dotted lines) show that surface reactions alone cannot account for full CH₄ conversion. About 25% CH₄ conversion is due to gas phase reactions sustained by the Pt-gauze due to release of heat and radicals.

References