

Experimental and numerical investigation of hydrogen production – higher hydrocarbons in catalytic partial oxidation

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Introduction:

Compact and autothermal reformers for the production of hydrogen and synthesis gas from liquid hydrocarbon fuels such as gasoline, diesel, and kerosene represent an efficient on-board technique for electricity supply via fuel cells (auxiliary power units, APU) as well as primary and secondary measures for reduction of NO_x emissions in conventional combustion processes [1]. Conventional fuels are attractive due to their high energy density, widespread production, and distribution and retailing infrastructure [2]. Furthermore towards reducing the dependency on limited fossil fuels, and increasingly utilization of regenerative fuels for automotive vehicles, the investigation and understanding of the performance of ethanol blends in catalytic partial oxidation (CPOX) reformers is necessary. The paper discusses experimental and numerical results for CPOX of gasoline surrogates and ethanol in a monolithic honeycomb structure coated with rhodium giving a better insight in the detailed chemistry and reactor performance.

Experimental:

The experimental setup allows well-defined accurate mixing of fuels with boiling points up to 280°C with synthetic air to feed the catalyst with a homogeneous, pulse free reactant flow and a uniform temperature profile. The product stream is analyzed by a variety of simultaneously applied methods such as FT-IR, MS and GC/MS allowing both a time resolved monitoring of the reaction and a fast screening of a diversity of fuel surrogates and gas mixtures [3].

Modeling:

The complex mixture of a large number of intermediates and radicals (over 200 chemical species) formed in the complex heterogeneous and homogeneous reaction network presents a challenge for the numerical simulation of detailed reaction kinetics in the coupling with flow description and transport phenomena. The approach is realized in the computer code for a two-dimensional flow problem DETCHEM^{CHANNEL} recently modified for the solution of large system of parabolic partial differential equations (PDEs) with nonlinear boundary conditions arising from the coupling between the gas-phase and surface processes [4].

Results:

Transient and steady-state investigations of CPOX with various gas phase compositions, fuel (C₆-C₁₂, aromatic hydrocarbons) and biofuel surrogates (ethanol blends) have been performed on Rh coated monoliths. A kinetic model was developed for CPOX of higher hydrocarbons for reformat / hydrogen production considering detailed mechanisms for the reactions in the gas phase and on the surface at transient and steady-state conditions. The heterogeneous chemistry is modeled by a set of elementary reactions representing the molecular behavior for the smaller hydrocarbons (C₁-C₃) and lumped steps for adsorption and destruction of larger hydrocarbons on the surface. The concept is applied to analyze conversion, selectivity, and temperature profiles in partial oxidation of iso-octane, a gasoline surrogate, over a rhodium/alumina monolithic catalyst. The interplay between heterogeneous and homogeneous reactions and the interaction in gas phase with and without surface chemistry were studied. Especially for fuel rich conditions, the homogeneous reactions play an important role [3]. The kinetic model was evaluated by comparison with experimental data as functions of operating temperature and C/O ratio. It could be shown that different hydrocarbon fuel surrogates show varying reaction behavior depending on their basic structure and chemical properties and take influence on both production of synthesis gas as well as formation of cracking products such as olefins and other coke precursors. Furthermore, additive species in the reformer inlet have been investigated with regard to hydrogen production and overall process enhancement. CPOX of ethanol blended fuels gives a first insight in the usability and the reaction behavior in such reformer processes.

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