

CATALYTIC PARTIAL OXIDATION OF HIGHER HYDROCARBON FUEL COMPONENTS AND SURROGATE MIXTURES ON RH/AL₂O₃

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Summary

Catalytic Partial Oxidation (CPOX) can be efficiently used for the autothermal conversion of logistic fuels to hydrogen and synthesis gas in compact reactors to supply portable and stationary fuel cells. In this paper, CPOX of characteristic constituents and test surrogate mixtures of logistic fuels are studied experimentally in Rh/Al₂O₃ coated honeycomb monoliths at short contact times. Towards a fundamental understanding, the role of the basic structure of the employed hydrocarbon is shown to dominate both production of synthesis gas as well as formation of cracking products such as olefins and other coke precursors. Based on the knowledge of the behavior of the different chemical constituents of logistic hydrocarbons reference fuels can be derived.

Keywords

Partial Oxidation, Hydrocarbon Fuels, Rhodium, Hydrogen.

Introduction

The catalytic partial oxidation (CPOX) of higher hydrocarbon fuels such as gasoline, kerosine and diesel allows the autothermal generation of hydrogen and synthesis gas for portable and stationary fuel cells via existing routes of supply [1, 2]. However, an optimization and reliable application of CPOX technology for fuel processing is calling for a better understanding of the complex interactions between gas phase and surface reactions in compact reforming reactors based on well-defined experiments as well as detailed modeling and simulation. The presented paper discusses new results for CPOX of gasoline and diesel fuel components and test surrogates surrogate mixtures on a monolithic honeycomb structured coated with rhodium.

Experimental Setup

The experimental setup enables the well-defined accurate mixing of hydrocarbon fuels with boiling points up to 280°C with synthetic air to feed the catalyst with a homogeneous, pulse-free reactant flow and ensures a uniform temperature profile. Moreover, up to 10 chemical species can be additionally feed into the reactor inlet flow for kinetic studies including H₂O, CO₂, H₂, CO or C₂H₄. The product stream is analyzed by a variety of simultaneously applied methods such as FT-IR, MS, GC/MS allowing a time resolved

monitoring of the reaction and therefore a fast screening of a variety of fuel surrogates and catalysts.

Results

Logistic transportation fuels are very complex mixtures consisting of many hundred hydrocarbons. Figure 1 compares the hydrogen yield produced by CPOX of various C₆ reference fuels and linear alkanes with different chain length in dependency of the C/O ratio.

All fuels show a maximum of hydrogen yield at a point slightly higher of syngas stoichiometry, i.e., C/O = 1.0. Under oxygen rich conditions, total oxidation is more favored involving the increased generation of water and carbon dioxide. As the C/O ratio is increased towards fuel rich conditions, the conversion of the hydrocarbon fuel generally decreases due to the limited supply of oxygen, whereas an increase of thermal decomposition (cracking) products is observed.

In dependence of the applied C₆ reference fuel, the maximum of hydrogen yield is reached at different C/O ratios, ranging from C/O = 1.0 to C/O = 1.1. Under fuel rich and fuel lean conditions, the shape of the hydrogen-yield curves is determined by the kind of fuel. Whereas n-hexane, i-hexane and cyclohexane show a comparable position of maximum and slope of that curve, considerably higher tendencies towards total oxidation are reached in conversion of the olefinic and the aromatic compound; at C/O = 0.8 hydrogen yield decreases to Y_{H₂} = 0.61 for benzene and Y_{H₂} = 0.67 for 1-hexene. In contrast to that result, linear hydrocarbons

achieve over a wide range of chain length a very similar behavior concerning H_2 yield as function of C/O ratio. All studied n-alkanes exhibit their maximum of hydrogen generation at the same C/O ratio of 1.05 and achieve almost the same hydrogen yield over the entire range of C/O ratios studied. Only a slight decrease in hydrogen yield is observed with increase of the linear chain. Hence, a slightly higher total oxidation is observed under oxygen rich conditions whereby under fuel rich conditions the thermal decomposition of the fuel (cracking) increases (also shown in Fig. 4).

The identification of the behavior of individual constituents of logistic transportation fuels allows the replacement of groups of hydrocarbons with similar properties by only a few hydrocarbons representing their average performance in CPOX reactions. Since gasoline, kerosene, and diesel are complex mixtures consisting of several hundred hydrocarbons, the reduction of the high complexity is considered as crucial for a better understanding of the interplay between the different components and their influence on important side reactions such the production of soot precursors, and water-gas shift, and steam reforming.

Conclusions

The developed experimental setup is designed for the investigation of complex reaction networks under defined boundary conditions and therefore supports the identification of important key reactions as well as the evaluation of a detailed kinetic model of catalytic partial oxidation.

In order to achieve a fundamental understanding of CPOX, our efforts start with single-component fuel surrogates such as i-octane and characteristic fuel components such as aromatic, naphthenic, olefinic and paraffinic species [3]. The interplay between heterogeneous and homogeneous reactions is explored in detailed transient and steady-state investigations by variation of C/O ratio, contact time, cell density and additionally in lean-rich cycles.

Based upon this analysis, multi-component fuel surrogates of logistic fuels were studied under various operation conditions regarding the production of synthesis gas and soot/coke precursors. Especially the handling of carbon deposition is expected to be crucial in technical applications since a long term operation without system regeneration is demanded. The role of the basic structure of the employed hydrocarbon is shown to dominate both production of synthesis gas as well as formation of cracking products such as olefins and other coke precursors. Based on the knowledge of the behavior of the different chemical constituents of logistic hydrocarbons reference fuels can be derived [4].

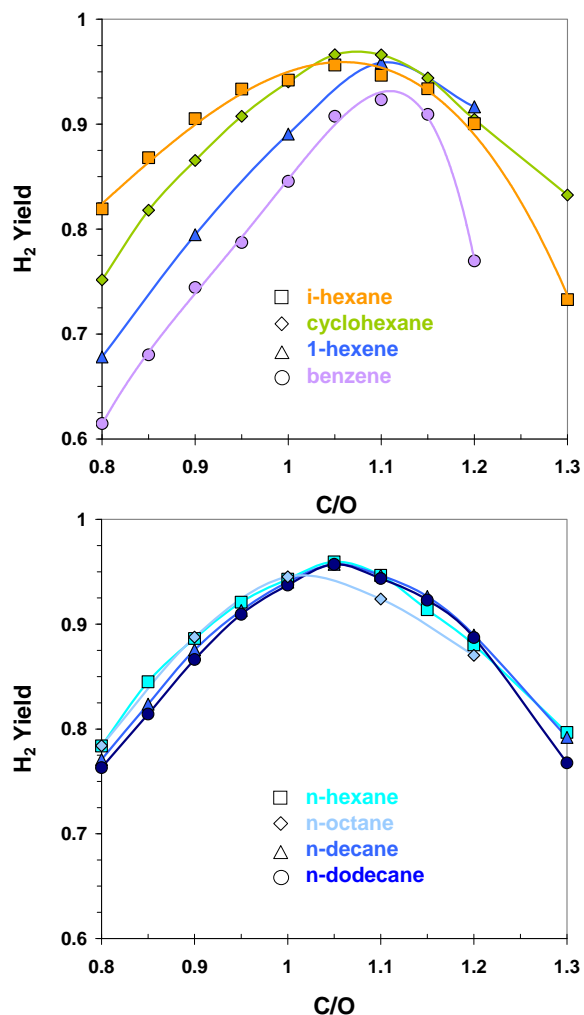


Fig. 1. Hydrogen yield by CPOX of various characteristic components of logistic transportation fuels in dependency of C/O ratios.

References

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