

CPOX OF I-OCTANE ON RH CATALYSTS AND EFFECT OF TAIL GAS FEEDSTOCK FOR HYDROGEN PRODUCTION

T. Kaltschmitt*, M. Hartmann and O. Deutschmann
Karlsruher Institut für Technologie (KIT), Kaiserstrasse 12, 76128 Karlsruhe, Germany

Summary

Catalytic partial oxidation (CPOX) of higher hydrocarbon fuels such as gasoline or diesel enable the generation of hydrogen or synthesis gas for on-site and on-board fuel cells via existing routs of supply. To achieve higher selectivities towards desired reaction products and to reduce coke formation of a fuel cell, tail gas is partly recycled into the reformer inlet. The present paper discusses the effect of carbon dioxide and steam to CPOX reformers with iso-octane as primary reference fuel. Gaining higher selectivities in synthesis gas production, tail gas recycling is reducing soot precursors up to 50 % and is therefore avoiding coke production downstream the catalyst, particularly in the fuel cell stack.

Keywords

Partial oxidation, Rhodium, Hydrogen production, Tail gas

Introduction

CPOX of logistic fuels such as gasoline or diesel offer a high throughput and autothermal route for the supply of large amounts of hydrogen for so called on-board auxiliary power units (APU) for mobile electricity production consisting of a reformer and a solid oxide fuel cell (SOFC) [1]. Raising prizes of limited energy sources make a more efficient use unavoidable. This demands a better understanding of chemical processes and detailed modeling. High yields and selectivities of hydrogen can be achieved using Rh coated catalysts in CPOX reactions [2]. For higher efficiency and long term stability of such APUs a fundamental understanding of the chemical processes is essential paving the way for commercialization. But not only efficiency is a major approach in industrial development, coke formation and emission control are also major challenges that have to be focused on. Refeeding the exhaust gas of a SOFC to the reformer inlet can be one possibility to reduce emissions and coke formation leading to an increase of the APUs efficiency which is of large industrial interest. By providing alternative C, H and O sources, a different reaction behavior is expected, influencing the reformer in regard to the mentioned major issues.

Therefore experimental investigations have been accomplished to point out the main effects of carbon dioxide and steam, the main products of a SOFC exhaust gas on a CPOX reformer. The deviations referring to iso-octane model fuel measurements without any addition

were determined and the impact on hydrogen production is presented. Modeling results supplement experimental data and give a better understanding in reaction chemistry. Kinetic studies reveal the effect of carbon dioxide and steam addition to the reformer forming a fundamental basis for detailed model approaches.

Experimental Setup

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 (3). 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 and Magnos allowing both a time resolved monitoring of the reaction and a fast screening of a diversity of fuel surrogates. Total flow determination is assured via drycal® technology and internal standard techniques.

Results and Discussion

CPOX reactions of higher hydrocarbons are ascribed by a large network of chemical reactions. In order to achieve a better understanding of tail gas addition into a CPOX reformer, investigations start by using a one component reference fuel feeding carbon dioxide or steam separately

* T. Kaltschmitt, Karlsruher Institut für Technologie (KIT). mailto: Torsten.Kaltschmitt@kit.edu

to the inlet. Figure 1 shows the increase in hydrogen molar flow rates up to 15 % comparing the reference fuel with steam addition. Considering the conversion of steam and carbon dioxide, steam takes more influence in the fuel lean and fuel rich range (about 75 % conversion) while carbon dioxide has its highest influence with about 50 % conversion in the lean area only (see Figure 2 + 3). The results show that both CO₂ and steam addition definitely affect the reaction performance but in a different modality indicated by the minimum for steam conversion at a C/O about 1.0. The oxygen in CO₂ and steam has a significantly different reactivity than oxygen in O₂. For this reason, characterization of reactants by means of C/O ratio only is not sufficient. Steam-to-carbon ratio and the amount of CO₂ have to be defined for a proper characterization of the reaction conditions as well as for coking propensity.

Regarding synthesis gas production, both carbon dioxide and steam take influence on the efficiency in a positive way. It can be shown that both additives lead to higher molar flow rates of hydrogen and carbon monoxide resulting in a higher supply of the SOFC with electrochemical fuel. As CPOX itself produces carbon dioxide and steam via total oxidation of the fuel, convenient conversions cannot be determined. The only possibility for a detailed understanding is due to numerical simulations. The amount of CO₂ and H₂O has to be considered, leading to differential conversions defined as

$$\Delta X = 1 - \left(\frac{\Delta n_{out}}{n_{in}} \right) \text{ while } n \text{ refers either to carbon}$$

dioxide or steam. with $\Delta n_{out} = n_{out}^{add} - n_{out}^{ref}$. More than one in parallel proceeding reactions could be identified for the production of hydrogen, e.g. steam and dry reforming and the (reverse) water gas shift reaction. Furthermore the reduction of soot precursors in both case studies leads to less coke formation and less hydrocarbon species reaching the SOFC, resulting in a better long term stability. All these aspects can be considered as a major challenge on the road towards bringing compact fuel processors to market.

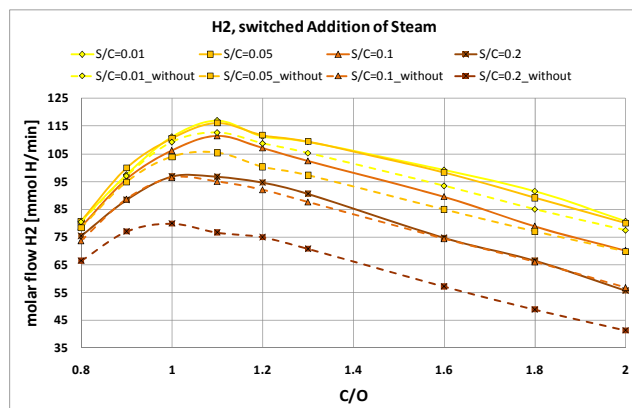


Figure 1: molar flow rates of hydrogen in case of steam addition and without steam addition.

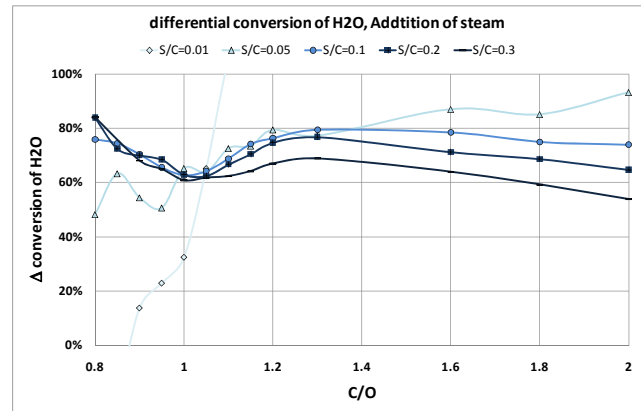


Figure 2: differential conversion of water in the CPOX reformer for different S/C ratios.

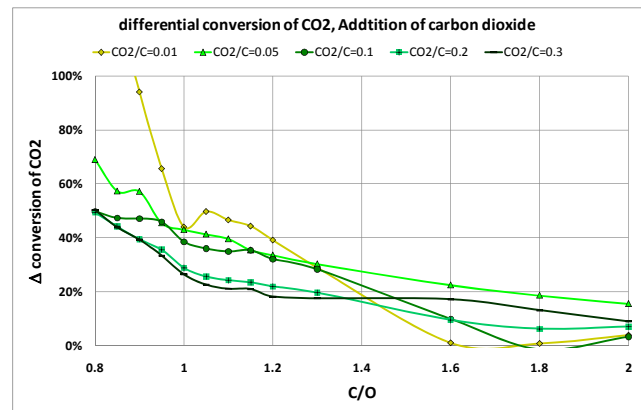


Figure 3: differential conversion of carbon dioxide in the XPOX reformer for different CO₂/C ratios.

References

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