Catalytic partial oxidation of higher hydrocarbon fuel components on Rh/Al$_2$O$_3$ coated honeycomb monoliths

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ABSTRACT

Catalytic partial oxidation (CPOX) can efficiently be used for the autothermal conversion of logistic fuels to hydrogen and synthesis gas in compact reactors to supply fuel for portable and stationary fuel cells. CPOX of characteristic constituents of logistic transportation fuels are studied experimentally in Rh/Al$_2$O$_3$ coated honeycomb monoliths at short contact times. Towards a fundamental understanding, the effect of the chemical structure of various hydrocarbon fuels on conversion and yield as well as the formation of coke precursors is investigated. Benzene, cyclohexane, 1-hexene and i-hexane are used to represent archetypically different classes of hydrocarbons in transportation fuels. The influence of the chain length of fuel components was evaluated by comparison of a series of linear alkanes ranging from n-hexane to n-dodecane. The effect of side chains of cyclic hydrocarbons has been studied by methyl substitution of benzene and cyclohexane. The role of the basic structure of the employed hydrocarbons is shown to dominate both production of synthesis gas and the 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.

1. Introduction

Reforming of logistic transportation fuels such as gasoline and diesel by catalytic partial oxidation (CPOX) to hydrogen or synthesis gas has gained significant attention due to its potential to provide the fuel for on-board and on-site fuel cells using the existing infrastructure [1–5]. Using rhodium catalysts, high yields of hydrogen ($Y_{H_2} > 90\%$) can be achieved at millisecond contact times upon low ignition temperatures [6–8]. Reliable long-term applicability of CPOX of logistic fuels calls for a better understanding of the complex interactions between gas phase and surface reactions, in particular the formation of coke precursors. A combined approach of both experimental studies and detailed modeling is expected to lead to a better understanding of the interaction of catalytic surface reactions, homogeneous gas-phase reactions as well as mass and heat transport.

Major experimental challenges for studying reforming of logistic fuels are: (i) complexity and variation of the fuel composition demand rapid screening of CPOX of many fuel components and mixtures, that means a rapid analysis of the product composition is needed to study many components and mixtures at varying parameters. (ii) Logistic transportation fuels are tailored to have optimum properties for their oxidation in internal combustion engines [9]. In order to achieve adequate ignition and combustion properties such as volatility, heat of combustion, freezing point, ignition delay time and so on, logistic transportation fuels are blended by mixing of distilled fractions of crude oil with processed streams of a refinery. Although their physical properties are regulated by several specifications, the chemical composition is varying within broad ranges, affected by the feed stock of the refinery or geographic/seasonal customization of the fuel. Fig. 1 gives an averaged chemical composition of the major logistic transportation fuels [10–12]. Consequently, the studies of the catalytic partial oxidation of logistic fuels is commonly restricted either on the detailed investigation of simple reference fuels such as i-octane or on parameterization of empirical models to describe reactor performance.

No comprehensive investigation concerning the performance and influence of different components of logistic transportation fuels have been published so far to the best of our knowledge. In order to reach a more fundamental understanding of the catalytic partial oxidation of higher hydrocarbon fuels, our efforts started with the detailed investigation of single-component reference fuels such as i-octane [13,14] and characteristic fuel components such as aromatic, naphthenic, olefinic and paraffinic species. Based

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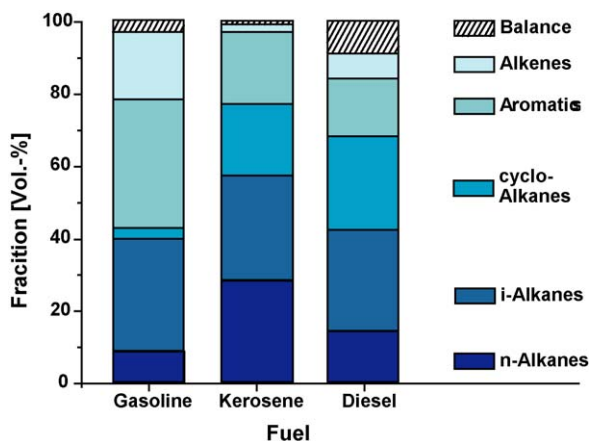E-mail addresses: Hartmann@ict.uni-karlsruhe.de (M. Hartmann), deutschmann@kit.edu (O. Deutschmann).

Fig. 1. Average chemical composition of logistic transportation fuels [10–12].

upon the knowledge of the reaction of characteristic fuel constituents, surrogates of logistic fuels can be derived. Besides the reduction of the high complexity of commercial fuels in model fuels, the use of surrogates allows a reliable standardization and easy reproduction of CPOX experiments. Moreover, the influence and interaction of dominant constituents can be explored, allowing the development of detailed models for CPOX of logistic fuels.

The objective of this work is the investigation of the significance of the chemical structure of hydrocarbons in CPOX over Rh based catalysts. Benzene, cyclohexane, 1-hexene, and i-hexane (3-methylpentane) have been chosen for the representation of archetypical constituents of logistic fuels. Since these species have the same number of carbon atoms, their performance can easily be compared using the molar carbon-to-oxygen (C/O) ratio. Furthermore, the influence of the chain length of fuel components is studied by comparison of a series of linear alkanes ranging from n-hexane to n-dodecane, representing the wide range of boiling points of the individual fuel components. Finally, the effect of side chains of cyclic hydrocarbons has been studied by using species with methyl substitution of benzene and cyclohexane.

2. Experimental and analytical setup

The experimental setup allows well-defined 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 ensures a uniform temperature profile. A detailed description of the reactor configuration is published elsewhere [13,14]. The fast mixing of the reactants in a flow reactor below auto ignition temperature is realized by a tube-in-tube system guaranteeing well-defined initial and boundary conditions. In addition, 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 large variety of fuel components and surrogates.

A commercially manufactured honeycomb catalyst has been used for the investigations. The monolith is made out of cordierite, 1 cm in length and 1.9 cm in diameter with a cell density of 600 channels per square inch (cpsi). The inner channel walls are coated with rhodium (load 4.23 mg/cm^3) dispersed on a γ-alumina washcoat; no further additives are used. The catalyst is positioned 20 cm downstream the mixture inlet. Upstream and downstream the catalyst, an uncoated foam monolith (Al$_2$O$_3$, 85 pores per linear inch, ppi) and an uncoated honeycomb monolith (600 cpsi), respectively, are placed close to the catalyst as flow homogenizer, heat shields, and fixations for thermocouples. The reactants are fed to the catalyst with 80% dilution in nitrogen, tempered at 190 °C at

a space velocity of 85,000 h^{-1}. For the initial preheating, the reactor is placed in a furnace, which is switched-off after ignition, hence the CPOX reactor then is operated autothermally. The deviation between measured catalyst outlet temperature and calculated adiabatic reaction temperature is between 25 and 75 K depending on the appointed C/O ratio, i.e. the deviation is less than 5% of the temperature increase due to chemical heat release.

The presented yield Y_P of the product species P is calculated in terms of the measured reactor outlet flow rates of molar carbon (C) or hydrogen (H) in the product species P divided by the molar inlet C or H flow rates of the fuel:

$$Y_P^H = \frac{\nu_P^H \dot{n}_P}{\nu_{Fuel}^H \dot{n}_{Fuel}^{In}} \quad \text{and} \quad Y_P^C = \frac{\nu_P^C \dot{n}_P}{\nu_{Fuel}^C \dot{n}_{Fuel}^{In}},$$

with $\nu_{P,Fuel}^{H,C}$ = number of H or C atoms in the product species P or in the fuel, $\dot{n}_{Fuel}^{In}$ and $\dot{n}_P$ = inlet fuel and outlet product molar flow rate. Hence, Y_P describes the molar distribution of carbon or hydrogen in the product spectra after the reaction.

3. Results

Fig. 2 presents the yield of hydrogen and water of the investigated C$_6$ reference fuels and linear alkanes in dependency of the C/O ratio. The sum of the yields of unconverted fuel and cracked hydrocarbons is displayed as C$_x$H$_y$. All fuels show a maximum hydrogen yield at a C/O ratio slightly higher than the one 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 C$_6$ reference fuel, the maximum hydrogen yield is reached at different C/O ratios, ranging from C/O = 1.0 to C/O = 1.1. The dependence of the hydrogen yield on the C/O ratio varies with the fuel. Whereas n-hexane, i-hexane, and cyclohexane show almost the same maximum hydrogen yield and C/O dependence, considerably higher tendencies towards total oxidation are reached in conversion of the olefinic and the aromatic compounds; at C/O = 0.8 hydrogen yield decreases to $Y_{H_2} = 0.61$ for benzene and $Y_{H_2} = 0.67$ for 1-hexene. In contrast to that, linear hydrocarbons reveal a very similar behavior concerning H$_2$ yield as function of C/O ratio over a wide range of chain length. All n-alkanes studied 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. 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 the thermal decomposition of the fuel (cracking) increases under fuel rich conditions (also shown in Fig. 4). The variation of the position of maximum synthesis gas production for different C$_6$ hydrocarbon fuels can be referred to the influence of steam reforming. If reactant stoichiometry reaches C/O = 1.0, additional synthesis gas is produced by the conversion of fuel with generated water as already had been shown for CPOX of light hydrocarbons over Rh and Pt [26,27]. On this account, the maximum of hydrogen yield is not located at the minimum of water production. In fact, the maximum of synthesis gas occurs simultaneously with a breakthrough of unconverted hydrocarbons recorded at the reactor exit. This result is in accordance with observations in transient lean-rich cycles of the CPOX of i-octane (unpublished results) and spatially resolved species profiles in the CPOX of methane [15].
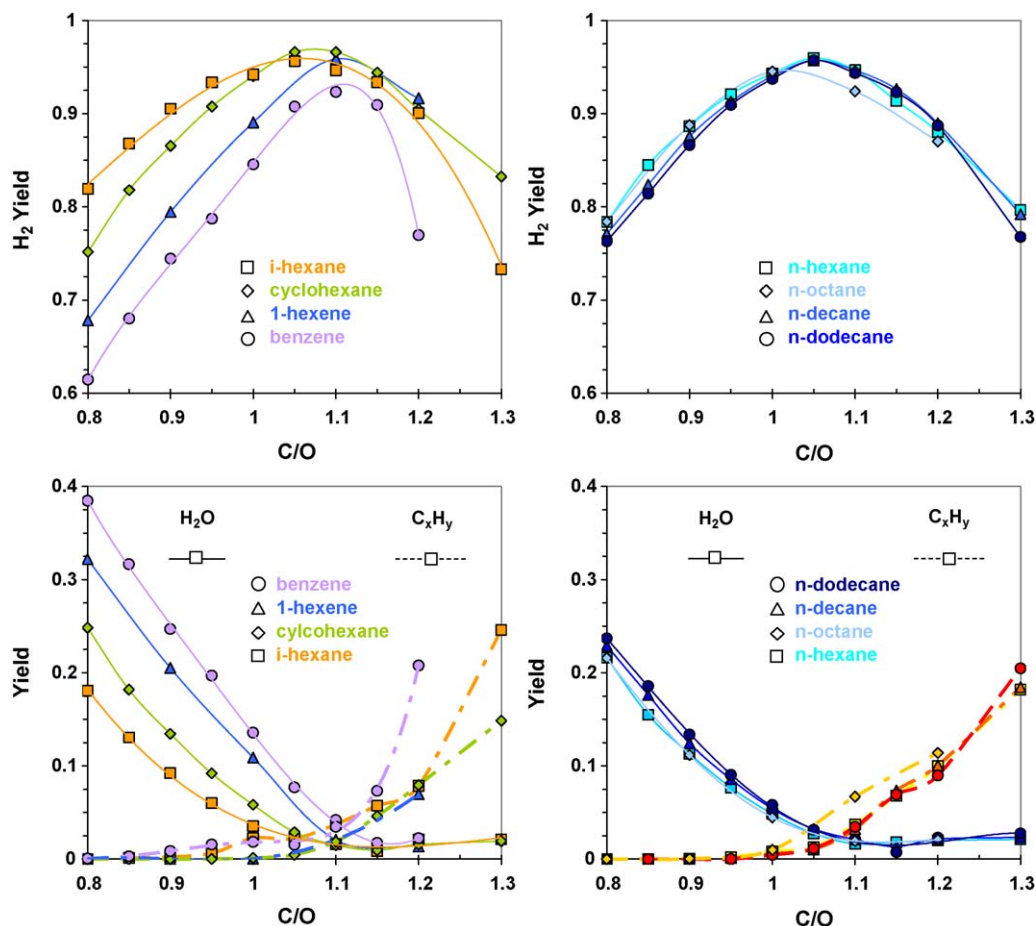
Fig. 2. H based H_2, H_2O, and C_xH_y yields in CPOX of characteristic components of logistic transportation fuels as function of C/O ratio. Upper panel: H_2, lower panel: H_2O and C_xH_y. C_xH_y denotes all hydrogen atoms containing products including unconverted fuel and thermal cracking products.

Fig. 3 shows the measured temperature at the catalyst outlet. In general, the temperature is increasing under oxygen rich conditions, evolving with the production of water referred to the highly exothermic total oxidation reaction. Under fuel rich conditions, for all fuels a slow decline of the catalyst exit temperature is recorded by the limitation of exothermic oxidation reactions. Based on the high selectivity to total oxidation, benzene reaches the highest temperatures exceeding 1250 °C at C/O = 0.8. Besides the selectivity to total oxidation, the fuel-dependent reaction enthalpies of total and partial oxidation determine the catalyst exit temperature. Due to the

aromatic system and the double bond, considerably higher reaction enthalpies (considering formation of syngas only) occur for benzene ($\Delta_R H^\circ = -746$ kJ/mol) and 1-hexene ($\Delta_R H^\circ = -621$ kJ/mol) in contrast to cyclohexane ($\Delta_R H^\circ = -539$ kJ/mol), and i-hexane ($\Delta_R H^\circ = -496$ kJ/mol). Therefore, the catalyst outlet temperature is determined by $\Delta_R H^\circ$ for syngas production at C/O $\sim$ 1.1 where all C_6-hydrocarbons are reaching comparable yields of hydrogen.

For the n-alkanes, a shift of the adiabatic catalyst outlet temperatures towards higher values is observed as a result of the increasing heat of combustion by increasing chain length. The shift
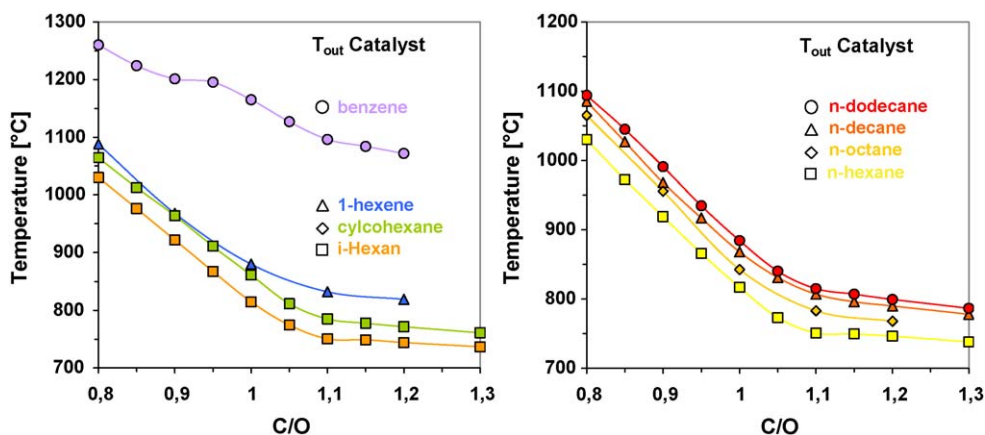

Fig. 3. Measured catalyst outlet temperatures in CPOX of various hydrocarbons fuels.
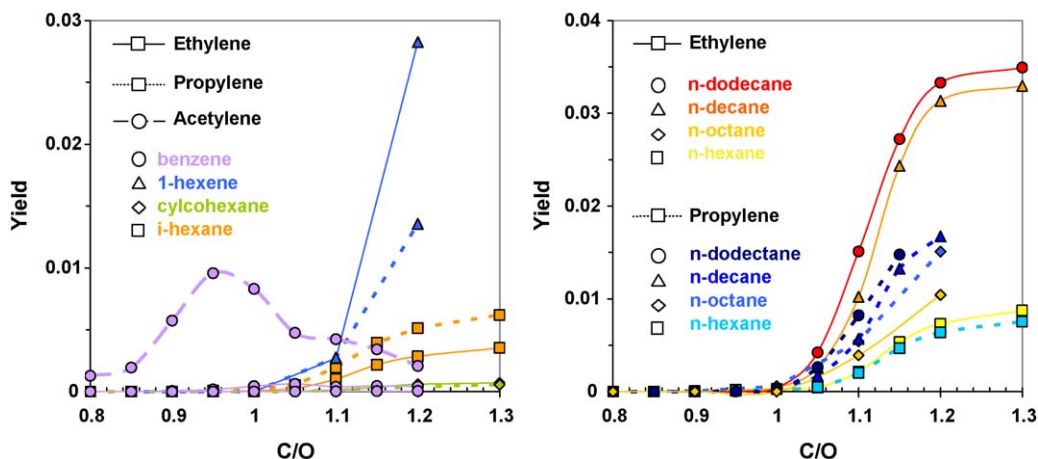
Fig. 4. C based yields of unsaturated hydrocarbons produced by thermal cracking of different C_6 hydrocarbons (left) and n-alkanes (right).

makes approximately 25 K for the addition of two CH_2 segments. Due to the almost identical dependence of hydrogen yield on C/O for all n-alkanes, a similar shift of the exit temperatures is measured. The effect of the increase in the heat of the combustion with increasing chain length exceeds the effect caused by the small reduction of the volumetric flow rate of the fuel with increasing chain length, which is needed to keep the C/O ratio constant at constant dilution and contact time.

Fig. 4 presents the production of the unsaturated hydrocarbons ethylene, propylene, and acetylene, which are likely to be produced by reactions in the gas-phase at rich conditions in the downstream part of the reactor where all oxygen is already completely converted [13]. Note that at all experimental conditions studied, oxygen conversion was always 100%. All cracking products are evolving with a breakthrough of unconverted fuel. Depending on the archetype of the hydrocarbon fuel, different amounts of cracking products are found, appear first (with C/O increasing) at different C/O ratios. While benzene does not produce a significant amount of α-unsaturated hydrocarbons, the n-alkanes do, and the olefine fuel (1-hexene) does even more. CPOX of cyclohexane leads to only minor amounts of ethylene and propylene, both below 100 ppm. The production of acetylene is only observed in conversion of benzene, caused also by the high temperatures in benzene conversion. Acetylene is the only hydrocarbon also produced under oxygen rich conditions, at C/O > 0.85. Regarding the n-alkanes, the similar formation rates of the olefinic cracking products indicate the same fragmentation scheme, which is in independent of the linear chain length [16]. Nevertheless, with an increase of the carbon backbone, an increased production of ethylene and propylene is recorded, also described by Fournet et al. [17]. Note that the yield to α-olefins is scaled by the number of carbon atoms of the fuel applied. The absolute concentration of ethylene is even more pronounced, from 900 ppm for n-hexane up to 5000 ppm at C/O = 1.3 for n-dodecane.

For all investigated fuels, production of methane occurs at syngas stoichiometry (C/O = 1.0) with concentrations up to 1000 ppm (not shown). Methane can be produced heterogeneously on the surface but also homogeneously in the gas-phase. Besides its production as a cracking product of paraffinic hydrocarbon species in the gas-phase under fuel rich conditions, it is also observed at lower C/O ratios above C/O > 0.9, at which no breakthrough of unconverted fuel is detected. This observation is linked to the reaction of adsorbed carbon atoms with adsorbed hydrogen both coming from heterogeneous fuel decomposition on the rhodium catalyst at the high reaction temperatures. At C/O = 1.0, a significant increase in methane generation is observed by

exclusion of the favored oxidation of surface carbon to CO or CO_2 according to the absence of excessive oxygen. The production of methane around C/O = 1.0 rather depends on the state of the catalyst than on the choice of fuel [6].

Fig. 5 shows the effect of attended side chains on the conversion of cyclic hydrocarbon fuels. Regarding the distribution of products, a minor variation can be observed by the addition of a methyl group. For the aliphatic and aromatic cyclic species, similar yields to syngas as well as a similar C/O ratio is observed for the onset of unconverted fuel breakthrough. At fuel rich conditions, no α-olefins are found in the product for benzene and cyclohexane as well as the methyl-substituted derivates. Temperatures at the catalyst outlet are increased by 30 K for both cyclic systems by oxidation of the methyl-substituted derivate. Acetylene is exclusively found in conversion of aromatic hydrocarbons. Furthermore, acetylene is the only hydrocarbon cracking product formed under fuel lean conditions, which can be dedicated to the high reaction temperatures reached in conversion of aromatic hydrocarbon fuels and by an excess of oxygen. As recently reported in literature, the formation of acetylene in CPOX can be assigned to the coupling of CH_3 radicals in the gas phase if high temperatures over 1300 °C are reached [18]. Ethylene production is observed at C/O > 1.0 as further coupling product with concentrations of approximately 50 ppm. However, since ethylene is an intermediate towards acetylene, its concentration is by an order of magnitude lower in comparison to acetylene.

All cyclic hydrocarbons show an increased carbon deposition on the walls of the reactor outlet tube in comparison to other tested hydrocarbon fuels such as 1-hexene and the n-alkanes: The coking occurs approximately 1–5 cm downstream the catalyst under fuel rich conditions, probably caused by condensation of cyclic and polyaromatic hydrocarbons leading to a fast agglomeration of soot particles [19–21].

4. Discussion

The presented study demonstrates the impact of the chemical structure on the catalytic partial oxidation of higher hydrocarbon fuels. The impact of intramolecular bonding on conversion and selectivity of paraffinic, olefinic, cyclic, and aromatic hydrocarbons, is superior to the impact of chain length and the presence of side chains on conversion and selectivity. Although, the chain length of the n-alkanes has been increased from n-C_6H_{14} to n-$C_{12}H_{26}$, reflecting a significant change in physical properties such as an increase of boiling point from 69 to 216 °C, only a negligible influence on the heterogeneous chemistry can be observed. In the same way, the addition of side chains has a minor effect on the
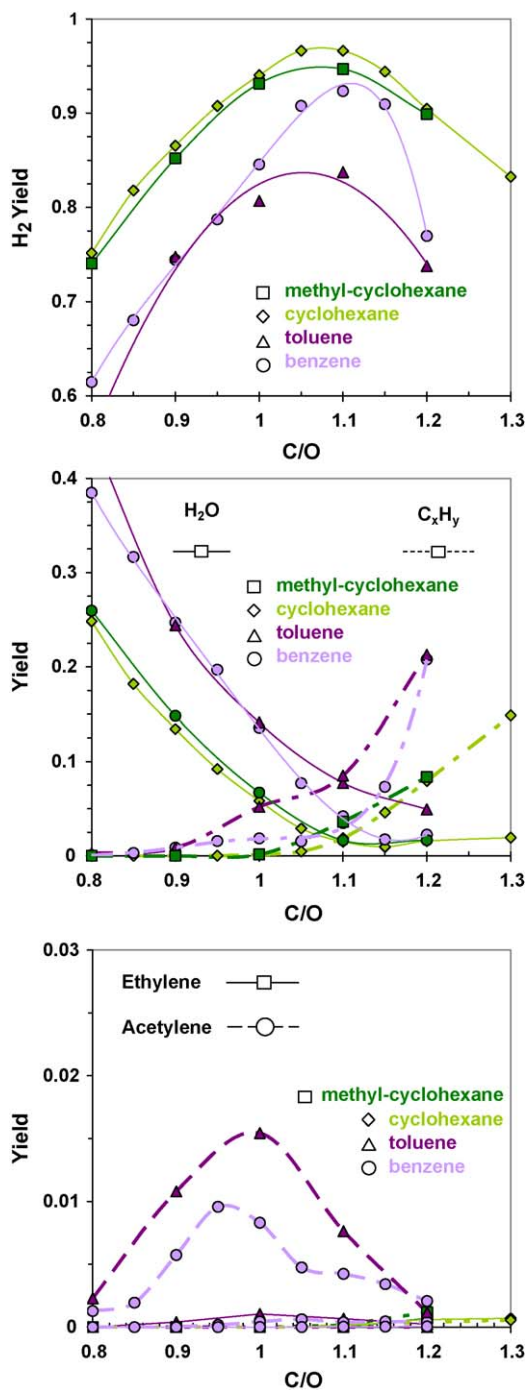
Fig. 5. H based yields in case of H_2, H_2O and C_xH_y (upper and middle figure) and C based yields in case of ethylene and propylene (bottom figure) in CPOX of methyl-cyclohexane, toluene, cyclohexane, and benzene.

towards thermodynamic equilibrium, the yields actually are relatively close to it, the results show a significant impact of the hydrocarbon structure of the fuel on the formation of different fragments by decomposition of the fuel on the rhodium surface.

For a technical application, a better comprehension of both quality and quantity of soot precursors generated in CPOX reactors is crucial [22–24]. The occurrence of soot precursors such as unsaturated α-olefins is also significantly determined by the chemical structure of the fuel. The observed soot precursors correspond to predictions by mechanistic studies of gas-phase decomposition of hydrocarbons at high temperatures in the absence of oxygen [16,17]. Each class of hydrocarbons has its intrinsic path of decomposition leading to a fragmentation pattern of favored cracking products. For example, cyclic hydrocarbons are dehydrogenated to polyaromatic hydrocarbons under CPOX conditions leading to a higher carbon deposit, whereas no ethylene or propylene production is observed. N-alkanes are decomposed by β-scission of alkyl radicals resulting in the production of short chained α-olefins [16,17,19,20]. The experimental investigations indicate that both chain length and side chains also have an (minor) influence on the quantity of the produced thermal cracking products.

The experimental setup used in the present study of CPOX of higher hydrocarbon fuels is able to guarantee well-defined boundary conditions and avoids gas-phase reactions upstream the catalyst, which has been a problem in the past [25]. Furthermore, the fast detection of the product gas composition assisted by FT-IR and MS enables the screening of various hydrocarbons with a high resolution of C/O ratios.

5. Conclusion

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 as their representatives in CPOX reactions. Since gasoline, kerosene, and diesel are complex mixtures consisting of several hundred hydrocarbons, the reduction of the high complexity is considered crucial for a better understanding of the interaction between the different components and their influence on important side reactions such as the production of soot precursors, the water–gas shift and steam reforming reactions.

The presented work reveals the dominant role of the structure of the hydrocarbon fuel (n-alkanes, i-alkanes, cycloalkanes, olefins or aromatics) on the production of synthesis gas as well as cracking products. Especially the presence of double bonds or an aromatic ring shifts the yield to total oxidation products. On the other side, over a wide range of boiling points, equivalent performance is observed for varying chain length of the hydrocarbon backbone or the appearance of side chains.

Model surrogates can be recommended representing the properties of logistic transportation fuels significant in CPOX and coke formation. First results with two and three component surrogates can reproduce conversion and selectivity in CPOX of commercially available gasoline.

Acknowledgements

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conversion of cyclic systems regarding total/partial oxidation products as well as cracking products. Besides the presented hydrocarbons, several additional hydrocarbons have been tested, supporting the general trend of the dominant influence of chemical structure on product distribution in CPOX over Rh. Furthermore, ambivalent behavior can be observed if hydrocarbons bear more than one characteristic attribute.

In general, the interaction of reactants with the catalytic surface is effected by the structure of the reactant molecule and is therefore playing a crucial role on its conversion. Even though, the high temperatures up to 1300 °C in general drive the product distribution

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