Potential of unwanted pre-reactions of LPG during the reforming processes in fuel cell CHP

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Abstract

LPG (liquefied petroleum gas) is an interesting fuel in the absence of natural gas concerning its low specific CO_2-emissions and high H/C-ratio. The combustion causes negligible soot, ash or particulate matter. Furthermore, it is allowed to use LPG in water and nature protected areas as well as in case of smog alert. LPG can be stored and transported easily at fairly low pressure. It has a high storage density, an interesting aspect for domestic and commercial applications as well as for island mode and camping.

CHP based on fuel cells are operated with hydrogen rich synthesis gas inter alia generated by steam reforming. A preheating of fuel up to the reaction temperature (650-750°C) is necessary for the reforming process. This is realized by integration of waste heat into the feed streams e.g. from cooling processes or exothermic reactions. Considering thermodynamic laws, maximum efficiency can be achieved in this way. Such measures are limited if LPG is used, because pyrolysis reactions occur accompanied with the production of a significant amount of olefins. In addition to the high temperatures, the potential rate of formation of these unsaturated hydrocarbons is increased by long residence times especially in partial-load operation. Olefins impair the function of catalysts for reforming processes by triggering the formation of carbon deposits on catalyst surface and reactor walls.

Prereforming is a well-known step to convert higher hydrocarbons into a methane rich gas before steam reforming takes place finally. But also in this case, a higher content of carbonaceous deposits is expected; especially if the used LPG contains a significant amount of olefins like propylene.

In the presentation the potential formation rate of unsaturated hydrocarbons by preheating LPG (>700°C) will be shown based on experimental measurements in comparison to published reaction mechanisms. Critical temperatures will be presented, which indicate the start of olefin generation. In this context, a distinction between an inert atmosphere and catalytic influences of tube and reactor wall is made. Furthermore, the influence of propylene (about 2 vol.-%) in commercial LPG on the formation rate of carbonaceous deposits on pre-reforming catalysts will be shown compared to pure propane. The supply of hydrogen to the feed may minimize carbonaceous deposits. In this context, the influence on deposits and on the overall efficiency of a fuel cell CHP by recirculation of synthesis gas will be shown.

1 Motivation

CHP based on fuel cells may constitute a future technology that generates and uses hydrogen from fossil fuels not only in medium-term, but also in long-term scenarios from synthetic natural gas (SNG) provided by technologies like Power-to-Gas. Total efficiencies up to 68% could be determined in case of coupling Power-to-Gas and reconversion into electrical and thermal energy by CHP [1]. One important prerequisite is a well-developed natural gas infrastructure, as it exists in Germany. However, not all regions are connected to the infrastructure especially rural settlements. LPG (Liquefied Petroleum Gas) can be an adequate substitute to meet advantages of a high efficient CHP based on fuel cell technology. This also applies low specific CO_2-emissions due to a high H/C-ratio compared to fuels like domestic fuel oil. The combustion causes negligible soot, ash or particulate matter. Furthermore, the use of LPG in water and nature protected areas as well as in case of smog alert is allowed. Another advantage is that LPG can be stored and transported easily at fairly low pressure. Additionally, the high storage density of LPG is beneficial for domestic and commercial applications as well as for island mode and camping.

A compact steam reforming system that generates a hydrogen-rich gas from LPG for CHP based on Low-Temperature-PEMFC was developed in cooperation with the company *DBI Gas- und Umwelttechnik GmbH*.

Figure 1: Left: Compact reformer system from *DBI Gas- und Umwelttechnik GmbH*, right: Fuel cell CHP *inhouse5000* from *Riesaer Brennstoffzellentechnik GmbH*

Currently, the reformer is installed in the inhouse5000, a CHP system based on Low-Temperature-PEMFC manufactured by the company *Riesaer Brennstoffzellentechnik GmbH* in Germany. The system is characterized by the following technical parameters:

Table 1: Technical parameters of the *inhouse5000*

LPG demand (reforming)	0.5 m³(N)/h		
Reformate gas stream	6.2 m³(N)/h		
Dry reformate composition	H_2	CO_2	CH_4
	75 vol.-%	23 vol.-%	2 vol.-%
CHP, electrical output	5 kW		
Alternation of load	30-100%		

The design of the compact reformer includes an optimized coupling of heat sources and heat sinks allowing the preheating of the feed gas, a mixture of fuel and water to the required temperature for the subsequent steam reforming process. Steam reforming is described as an endothermic reaction in

which hydrocarbons and steam react to hydrogen and carbon monoxide according to

$$C_nH_m + n\,H_2O \rightarrow n\,CO + \left(n + \frac{m}{2}\right)H_2 \qquad\qquad \Delta_R H^0 > 0$$

<div align="right">Equation. 1</div>

In parallel, carbon dioxide is formed by the Water-Gas-Shift reaction:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad\qquad \Delta_R H^0 = -41{,}2\,\text{kJ/mol}$$

<div align="right">Equation. 2</div>

The ratio of process water to fuel is described by the steam-to-carbon ratio:

$$\dfrac{S}{C} = \dfrac{\dot{n}_{H2O}}{x \cdot \dot{n}_{CxHy}}$$

<div align="right">Equation. 3</div>

In general, a higher S/C-ratio than the required stoichiometric ratio is adjusted in the process. This leads to higher hydrogen yields and a lower affinity towards catalyst deactivation due to carbonaceous deposits.

To achieve a CO- level of less than 10 ppm in the final gas mixture the hydrogen-rich gas generated in the steam reforming process is cooled and a Water-Gas-Shift and a Preferential-Methanation step are applied.
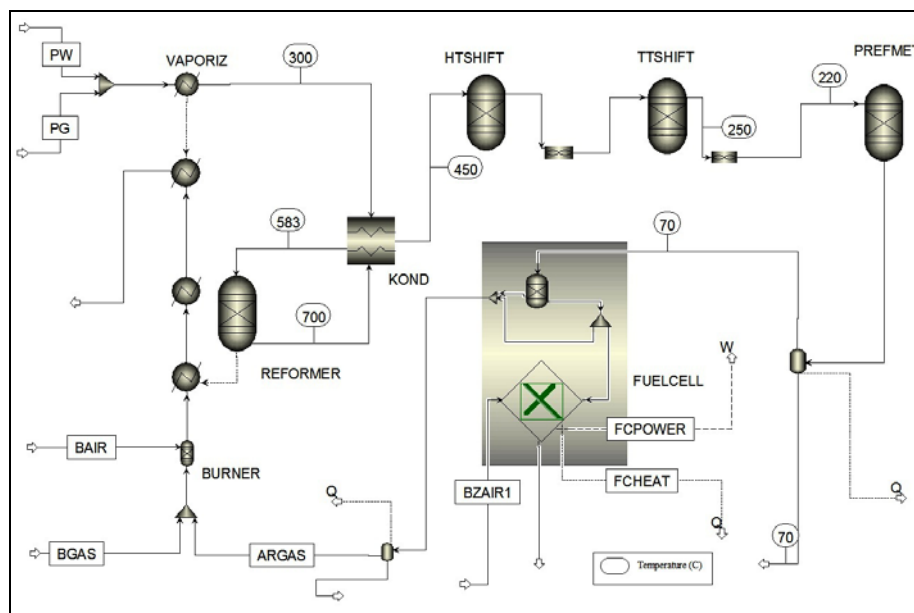

Figure 2: ASPEN PLUS flow sheet of the *inhouse5000* system

Preheating up to reforming temperatures in the range of 650°C to 700°C is unproblematic in case of a reformer feed gas composition of methane and steam. However, preheating is limited when higher hydrocarbons like LPG are going to be used due to the thermodynamic instability of the major components propane and butane at temperatures above 100°C-150°C. The preheating of LPG results in unwanted prereactions coupled with a significant formation of unsaturated hydrocarbons like propylene and ethylene. These gaseous species promote the formation of carbonaceous deposits leading to the premature deactivation of the reforming catalyst. The aim of the present work was the detailed under-

standing of the formation potential of unsaturated hydrocarbons in the compact reformer system depending on parameters such as preheating temperature and residence time. Furthermore, strategies to avoid the formation of carbonaceous deposits in the reformer were developed in compliance with the technical requirements of a fuel cell CHP.

2 Carbonaceous deposits on reforming catalysts

Three main forms of carbonaceous deposits are distinguished on reforming catalysts: polymeric and filamentous deposits and pyrolytic carbon.

Polymeric deposits, „Gum"

Polymeric deposits result in encapsulation of the catalytic active surface by polymerization of adsorbed higher and unsaturated hydrocarbons [2]. The formation is preferred in case of imbalance between adsorption and conversion rate of the hydrocarbons by gasification at low temperature levels especially in prereforming processes. Through this, hydrocarbon fragments accumulate more and more on the catalyst surface and form a polymeric non-reactive film [3]. In general, low temperatures, low steam-to-carbon-ratios and high contents of aromatic and/or unsaturated hydrocarbons promote polymeric deposits [4, 5].

Filamentous deposits, „Whisker"

Carbon filaments are very common on reforming catalysts. They occur preferentially on Nickel-based catalysts due to hydrocarbon or carbon monoxide dissociation on the catalytic active metal particles [6] combined with desorption of molecular hydrogen. The formation of whisker can be described by diffusion of carbon atoms under the nickel crystals following growth of carbon filaments with the nickel crystal on the top. The structure dimensions are 0.1-1000 µm length and 3-100 nm diameter [7]. Whiskers are characterized by a high chemical stability leading to damage of catalyst particles. Finally, maldistribution of the gaseous fuel occurs resulting in local hot spots and damage of the reformer wall material. Parameters that promote whisker formation are low steam-to-carbon-ratios, high temperatures as well as high contents of aromatic and unsaturated hydrocarbons in the feed [3].

Pyrolytic carbon

Pyrolytic carbon is formed by thermal cracking of hydrocarbons in the gas phase at temperatures higher than 600°C. The mechanism is complex and starts with the formation of unsaturated molecules and radicals that react furthermore by polymerization and dehydrogenation. Condensing of resulting macromolecules follows by increasing partial pressure, finally, on the on-going dehydrogenation leads to the formation of solid soot [3].
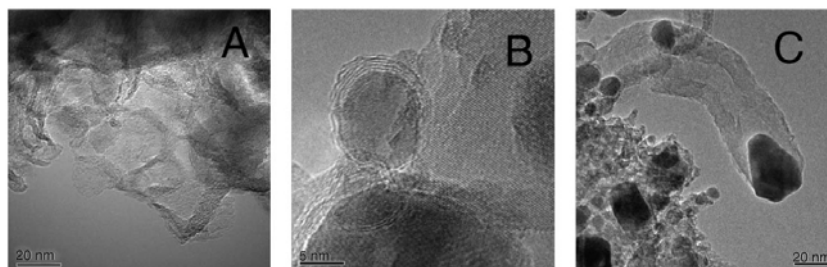

Figure 3: Electron microscopy images of (A) pyrolytic carbon, (B) encapsulating carbon, and (C) whisker carbon on Ni/MgAl$_2$O$_4$ reforming catalysts [8]

3 Potential of unwanted prereactions

The unsaturated hydrocarbon formation rate during the preheating process of propane was studied numerically as well as experimentally. Numerical investigations were carried out using the software package *Chemkin 4.1.1* based on published reaction mechanisms that were developed for pyrolysis and combustion of hydrocarbons. The experimental setup consists of a plug-flow-reactor that has an inner quartz glass tube to avoid unwanted reactions of the process gases with the metal wall and that can be heated up to the desired temperatures. The feed gases were supplied via thermal mass flow controllers. Gas samples were taken at different axial positions of the reactor via a sampling probe and their compositions were analyzed using gas chromatography. The following figure shows the propane conversion depending on the reactor temperatures for both experimental and numerical investigations. The numerical results were achieved by using the measured reactor temperature profile ensuring the same conditions in experiment and numerical model.
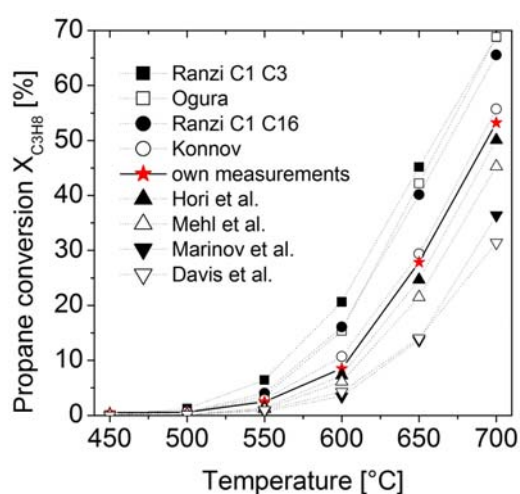

Figure 4: Comparison of published mechanisms and experimental results

None of the mechanisms was evaluated for its suitability for propane pyrolysis in the temperature range of 450°C to 700°C. The results for the propane conversion differ significantly, however, the results of own measurements are located in the middle. Published mechanisms according to *Konnov et al.* [9] and *Hori et al.* [10] represent almost the qualitative trend of the experimentally determined conversion.
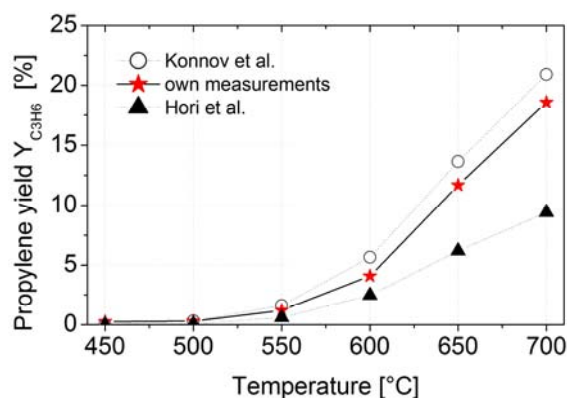

Figure 5: Propane pyrolysis, propylene yield, comparison of own measurements with the mechanisms of *Konnov et al.* and *Hori et al.*

However, there are strong differences in relation to the gas composition particularly for the primary products propylene and ethylene caused by different kinetic parameters of the mechanisms, as shown in Figure 5 exemplarily for propylene.

The following figure shows the progress of the main species that are formed during the pyrolysis when preheating of propane from ambient temperature to 700°C. A high content of ethylene and propylene can be clearly observede at long residence times, resulting in14 vol.-% at 2 s and 35 vol.-% at 13 s, respectively.
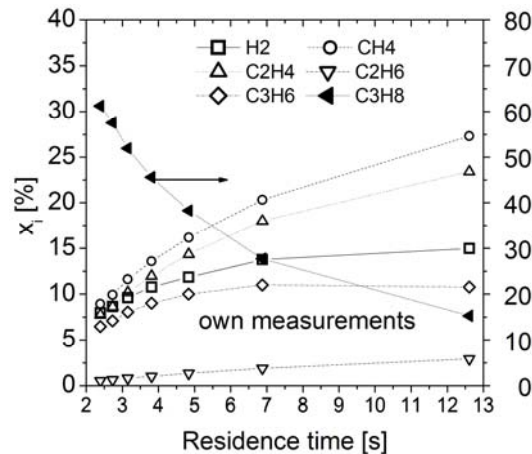

Figure 6: Heating of C_3H_8 (700°C): Product gas composition as function of residence time

Depending on the partial-load operational range of the compact reformer a residence time up to 8 s can be expected during preheating of the fuel. This describes an unacceptable value related to the formation rate of unsaturated hydrocarbons, because the formation of higher carbonaceous deposits results in the premature deactivation of the catalyst. To avoid that, a prereforming step was integrated into the system enabling the conversion of the LPG/steam-mixture at lower temperatures (350°C-550°C). Therefore prereactions and carbonaceous deposits are minimized and the formation of pyrolytic carbon is avoided.

4 Temperature-Programmed-Methanation (TPM)

Another source of unsaturated hydrocarbons like propylene is the LPG itself. Own investigations have shown propylene contents up to 4 vol.-% in commercial LPG. Temperature-Programmed-Methanation (TPM) was used to demonstrate that this content can promote higher carbonaceous deposits on a prereforming catalyst compared to pure propane. TPM is realized by addition of a constant hydrogen flow over the catalyst in conjunction with a linear temperature increase. Hydrogen and carbon react to methane that can be analyzed.

$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H_R\text{=-75 kJ/mol} \qquad \text{Equation} \quad 4$$

The method is well-described in the literature and offers the opportunity to distinguish different forms of carbonaceous deposits. For own experimental investigations identical catalyst samples were exposed to different feed gas compositions in prereforming mode at 450°C. The compositions were pure methane, pure propane and a commercial LPG composition with propylene content of 3.6 vol.-%. The applied boundary conditions were the same for all tests: Steam-to-carbon-ratio = 4.0; GHSV = 12000

1/h. Finally, the samples were investigated by TPM with a constant hydrogen flow of 4 l/min and a linear temperature increase of 5 K/min. In figure 7 four characteristic peaks are clearly observed that can be attributed to various carbonaceous species. On the basis of the associated temperature range, a decreasing reactivity with increasing temperature can be stated. Furthermore, it is obvious that the structures at higher temperatures are more graphitic. The first peak (450°C-550°C) describes adsorbed CO_2-Species as intermediate that can be found at all reforming processes. Peak 2 (520°C-570°C) and peak 3 (550°C-650°C) are related to polymeric deposits ("gum"), whereby filamentous carbon ("whisker") is excluded due to the low reforming temperature. In general, a higher content of deposits is clearly observed when using propane and commercial LPG compared to methane. The overall area under the graph of LPG is obviously the largest, which implies higher carbonaceous deposits on catalysts by using commercial LPG with low propylene content compared to pure propane. This results in a shortening of the catalyst life time.
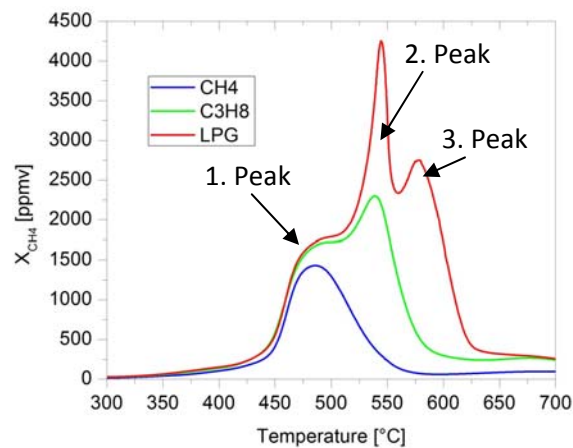

Figure 7: Results of the Temperature-Programmed-Methanation (4 l/min H_2, linear temperature increase 5 K/min)

5 Hydrogen refeeding

In addition to temperature, pressure, S/C-ratio and catalyst properties feed composition influences also the potential of carbonaceous deposits. The selective addition of hydrogen can minimize carbonaceous deposits whereas unsaturated hydrocarbons in the feed influence negatively the process. Industrial applications like steam reforming of naphtha contain a preforming step including refeeding of hydrogen-rich synthesis gas from main reformer. This leads to hydrogenation of carbonaceous deposits, lower deactivation rates and longer catalyst life time are achieved. [3]

Hydrogen is produced primarily for the fuel cell stack operation in the inhouse5000 system described before. Not the complete hydrogen can be used in the stack due to technical and physical reasons resulting in a hydrogen-containing offgas (H_2 about 35 vol.-%) that is fed into a burner for thermal conversion. The offgas can be recycled theoretically into the reforming process. However, this influences the overall system behavior significantly. First, offgas is detracted from combustion resulting in additional required fuel; second, a change in thermodynamic equilibrium of the steam reformer occurs by additional hydrogen and carbon dioxide from the offgas. In summary, changes in overall efficiency and fuel demand occur. The behavior of the whole system that is influenced by variable recirculation of stack offgas was determined by using a one-dimensional energy and material flow model in *ASPEN PLUS®*. Offgas was splitted step by step under a constant electrical power of 3 kW and fed partially into the steam reforming process (see figure). In case of refeeding into the reformer the ratio of H_2/C_3H_8 increases resulting in lower process gas demand because the required hydrogen for constant

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stack power is covered partially by offgas. In return, burner fuel demand increases, because of less offgas. The electrical net efficiency increases slightly until an offgas split ratio of 30-40% is achieved. This point corresponds to a H_2/C_3H_8-ratio of about 1. A further increase in the split ratio results in a decreased efficiency.

In a long-term test over 24 h the decrease of conversion at similar catalyst samples by using different feeds during prereforming was investigated. The feeds were pure propane, commercial LPG (3,6 vol.-% propylene) as well as a mixture of commercial LPG and H_2 (1/1). Results are shown in Figure 9 by ratio of conversion at the time t to conversion at beginning t_0.
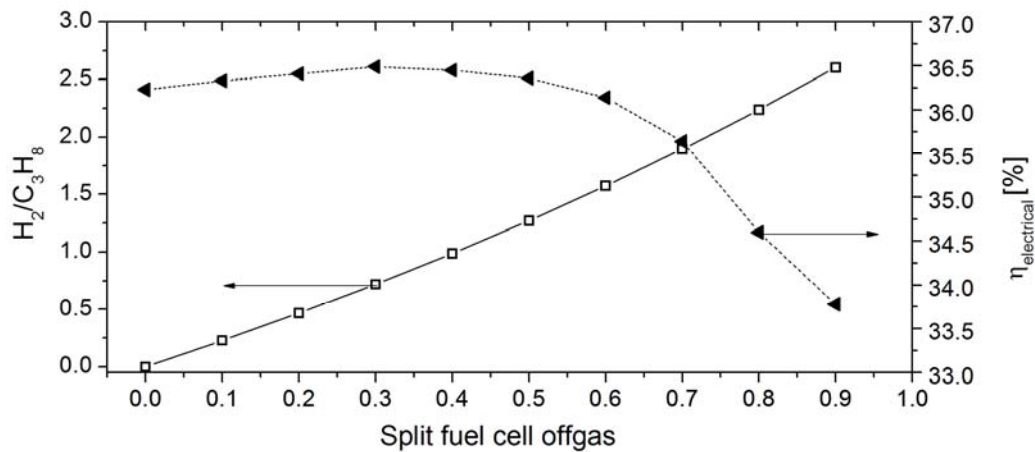

Figure 8: Electrical efficiency and H_2/C_3H_8-ratio dependent on split fuel cell offgas system inhouse5000 (electrical output 3 kW, reformer temperature = 700°C, S/C-ratio = 4.0)
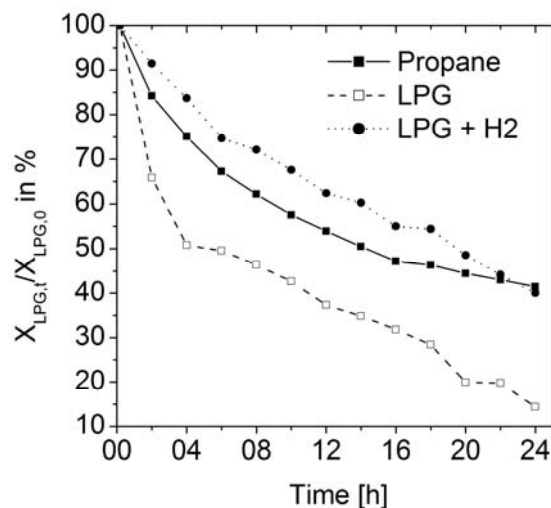

Figure 9: 24h-steam reforming, comparison of conversion of different feed

A decline in conversion can be found in all experiments. This is most pronounced in case of commercial LPG due to the propylene content. Decline of conversion is reduced by addition of hydrogen caused by hydrogenation of adsorbed hydrocarbon fragments and carbon deposits.

6 TPM-investigation at catalyst exposed to LPG/H₂-mixture

The positive influence of a hydrogen addition can be demonstrated by TPM as well.
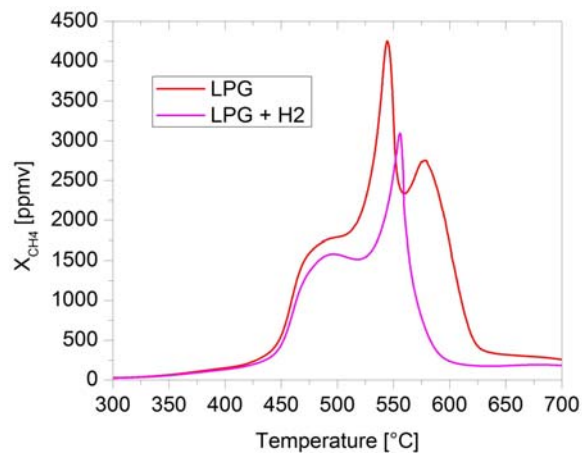

Figure 10: TPM-results show lower carbon deposits by H₂-addition to feed

Therefore, a prereforming sample was exposed to the LPG/H₂-mixture (1:1) under the same boundary conditions described before. Finally the sample was examined by TPM. The decline of the area under the graph for the LPG/H₂-mixture compared to LPG is clearly visible. Using TPM also shows the positive influence of hydrogen refeeding in addition to the long-term tests. The amount of carbonaceous deposits is reduced.

7 Summary

The formation of unsaturated hydrocarbons is promoted by long residence times during the preheating of LPG up to typical reforming temperatures. This affects the utilized reforming catalysts because carbonaceous deposits are formed in larger amounts leading to premature deactivation of the catalyst. Integration of a prereforming step can reduce significantly the formation potential. Furthermore, measurements via long-term test and Temperature-Programmed-Methanation show that even small amounts of propylene in LPG decrease the amount of carbonaceous deposits. From a technical perspective, the use of propane would be the best solution. However, this is not economically feasible due to very high production costs. LPG compositions vary regionally and seasonally particularly in propylene contents. The addition of hydrogen by recirculating offgas in fuel cell CHP reduces carbonaceous deposits and the reformer life time can be extended. Furthermore, summarized results show that less process gas is necessary for the same electrical output of the CHP whereby the catalyst is exposed to less carbon containing feed and the life time of the catalyst is extended.

Abbreviations

CHP   Combined heat and power

LPG   Liquefied Petroleum Gas

PEMFC   Proton Exchange Membrane Fuel Cell

TPM   Temperature Programmed Methanation

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