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Reforming of diesel fuel in a micro reactor for APU systems

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Abstract

Reforming of diesel fuel in micro reactors is a challenging but very attractive way for converting conventional fuel in a hydrogen rich gas for fuel cells applied for electrical energy generation, e.g. in auxiliary power units. To understand diesel reforming and to compare the process with reforming of other substances, the reforming of possible diesel conversion intermediates (methane and propane) and of a first diesel surrogate, hexadecane, was examined isothermally in a microchannel reactor in this study using rhodium as catalyst. The product analysis was established with a special method on a gas chromatograph to analyse all substances in one run. It was observed that branched feed molecules are converted faster on the rhodium catalyst than the unbranched molecules, latter ones exhibiting a reciprocal dependency of turnover frequency on carbon atoms per molecule. These observations are a first hint for the kinetics of the reforming. In higher hydrocarbons the $-$CH groups seem to be converted more easily than $-CH_2$. C$-$C bonds seem to be converted in an adsorbed state of both C due to the reciprocal dependency and due to negligible byproduct formation. Moreover, the negligible byproduct formation and the reciprocal dependency lead to the assumption that most of the conversion in the microchannels is performed on the catalyst surface and not in the gas phase.

Keywords: Steam reforming; Diesel fuel; Gas chromatography; Microchannel reactor; Catalysts

1. Introduction

Reforming of diesel fuel is a challenging method of hydrogen production but it is also very attractive. The reforming in micro reactors has several advantages over conventional reactors. As a catalytic reaction is studied, the ratio of active catalytic surface to reactor volume determines the reactor/system dimensions. Large surface to volume ratios are necessary for designing small and compact fuel processing systems for mobile fuel cell applications. The use of microchannels enables to maintain isothermal conditions in the reforming reactor due to extensive heat management possibilities. Heat supply can easily be coupled with reforming channels by locating these channels adjacent to heat exchanger channels or to channels with an exothermal combustion reaction and hence providing stable temperature conditions within the reactor volume.

Diesel or gasoline will be the preferred feeds for electrical energy generation, e.g. in auxiliary power units (APU). With these APU systems the increasing electrical power demand in heavy duty trucks and passenger cars can be met independently of engine operation [1].

Fuels such as natural gas, methanol, propane or gasoline have been widely studied for their reforming characteristics [2,3]. Due to the complexity of diesel fuel, its conversion by steam reforming causes more problems. Therefore reforming of different diesel components and conversion intermediates in a microchannel reactor is investigated systematically in a test rig at the Institute for Micro Process Engineering. The results presented are obtained by using a test reactor which is electrically heated and contains exchangeable micro structured reformer foils. These experimental results will lead to the design of a so-called system reactor, which shall incorporate catalytic combustion channels adjacent to reformer channels for providing a high thermal integration of the system.

2. Experimental

2.1. Test rig and reactor

The test rig, shown in Fig. 1, provided premixing of hydrocarbon, oxygen and nitrogen feeds in a micro mixer and subsequent reaction with steam in a heated microchannel reactor.

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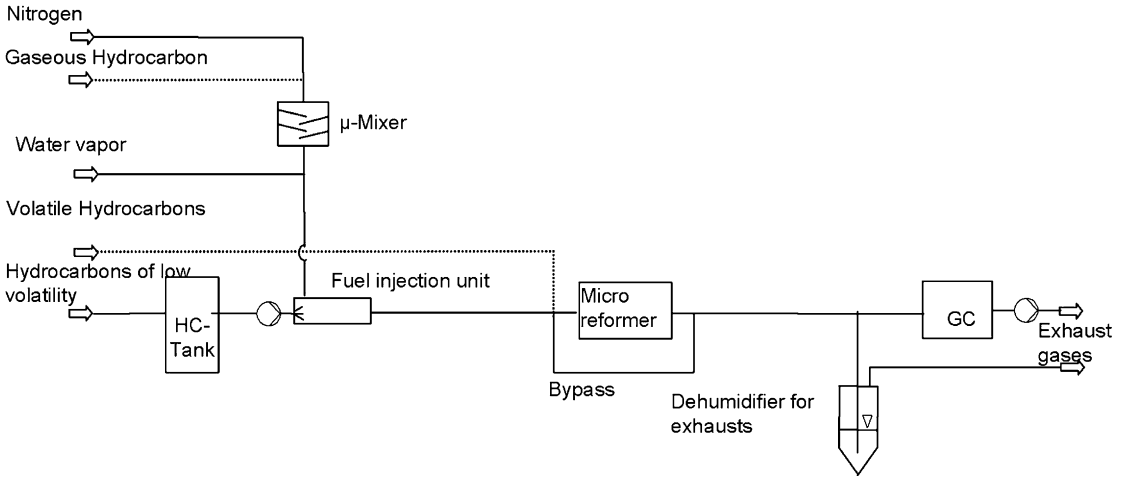

Fig. 1. Reaction scheme of test rig for diesel reforming experiments.

Nitrogen gas and gaseous fuels (methane and propane) were fed by mass flow controllers from Brooks into a V-type micro mixer [4]. Although oxidizing conditions are not under investigation in this paper the micro mixer was implemented in the test rig to reduce the risk of explosion when feeding additional oxygen. For hydrocarbon fuels with low boiling points up to 180 °C, i.e. isooctane, the fuels were evaporated in a heated pressure vessel and fed to the micro mixer by heated mass flow controllers from MKS. Steam was produced and supplied in the same way as isooctane. Hydrocarbon fuels with higher boiling points, i.e. hexadecane were sprayed through a microstructured nozzle and evaporated in the overall steam and nitrogen premix. The premix of hydrocarbon and steam was fed to the microchannel reactor or directly into the gas chromatograph by a bypass beneath the microchannel reactor for determination of product or reactant composition respectively.

The microchannel test reactor was filled with 14 micro structured foils. 200 μm × 200 μm square microchannels were machined in Nicrofer foils. Each foil contained 100 channels of 80 mm length which results in a geometric surface area of 6360 mm^2 including the top of the fins, i.e. the coated surface on top of the foil. This is calculated on this basis because clamping microstructured foils cannot prevent gas contact to this catalyst region. The temperature of the reactor was controlled using eight heat cartridges, four on top and four on the bottom of the foil stack. The four heat cartridges on top and on bottom of the foil stack were controlled in one heat circuit each. Nearly isothermal conditions by high heat conductivity of the foil stack were proven to be valid within measurement accuracy by a moveable thermocouple positioned in the middle of the stack.

2.2. Catalyst preparation

All experiments were performed over a rhodium catalyst supported on a layer of alumina. Thus, the micro structured foils were, first, coated with alumina, Al_2O_3, by sol–gel technique for surface extension purposes [5]. The solution was equally distributed over the top surface of each foil, dried at 70 °C over night and, finally, calcined at 800 °C for 5 h in air. Afterwards, rhodium was deposited on the aluminum oxide layer by impregnation of the foils with aqueous $RhCl_3$ solution in the same manner. Again, the impregnated foils were dried and calcinated at the same conditions as before. Due to weight control of the distributed solution of alumina and rhodium each foil was coated on average with 2.7 mg Rh and 10 mg Al_2O_3 with a small standard deviation of 2.5% and 13%, respectively. The whole reactor contained about 40 mg of rhodium. Before performing any experiments in the micro reactor, the reaction foils were reduced in situ at 750 °C in 2 vol% of hydrogen in nitrogen.

The thickness of coating layer of alumina and rhodium on the metal was determined to be 2–3 μm by embedding the samples in Araldit® resin, cutting and polishing the samples and taking photomicrographs and SEM of the cross-section of the foil. For further examination of the catalyst support system, the BET surface area was determined with an Autosorb 1 (Quantachrome) with nitrogen and a detection limit of 1 m^2. The surface area of the coated foils was also expressed in terms of an enhancement factor F, defined by the ratio of the product of the measured BET surface area (m^2/g) and the coating weight (g) to the geometrical surface area of the foil (m^2). Chemisorption experiments with the adsorbate hydrogen were performed in the same apparatus to get information about the catalyst dispersion. The dispersion is defined as the ratio of the number of active sites Rh to the total number of Rh atoms.

2.3. Analysis method

The micro reactor product gas was analysed with a gas chromatograph (GC) model 6890 from Agilent. The GC was equipped with flame ionization (FID) and thermal conductivity (TCD) detectors, and three capillary columns: HP1, PlotQ, and molsieve. To analyse concurrently hydrocarbons up to C_{16}, permanent gases (hydrogen, nitrogen, oxygen, carbon monoxide and methane) and carbon dioxide, the GC flow

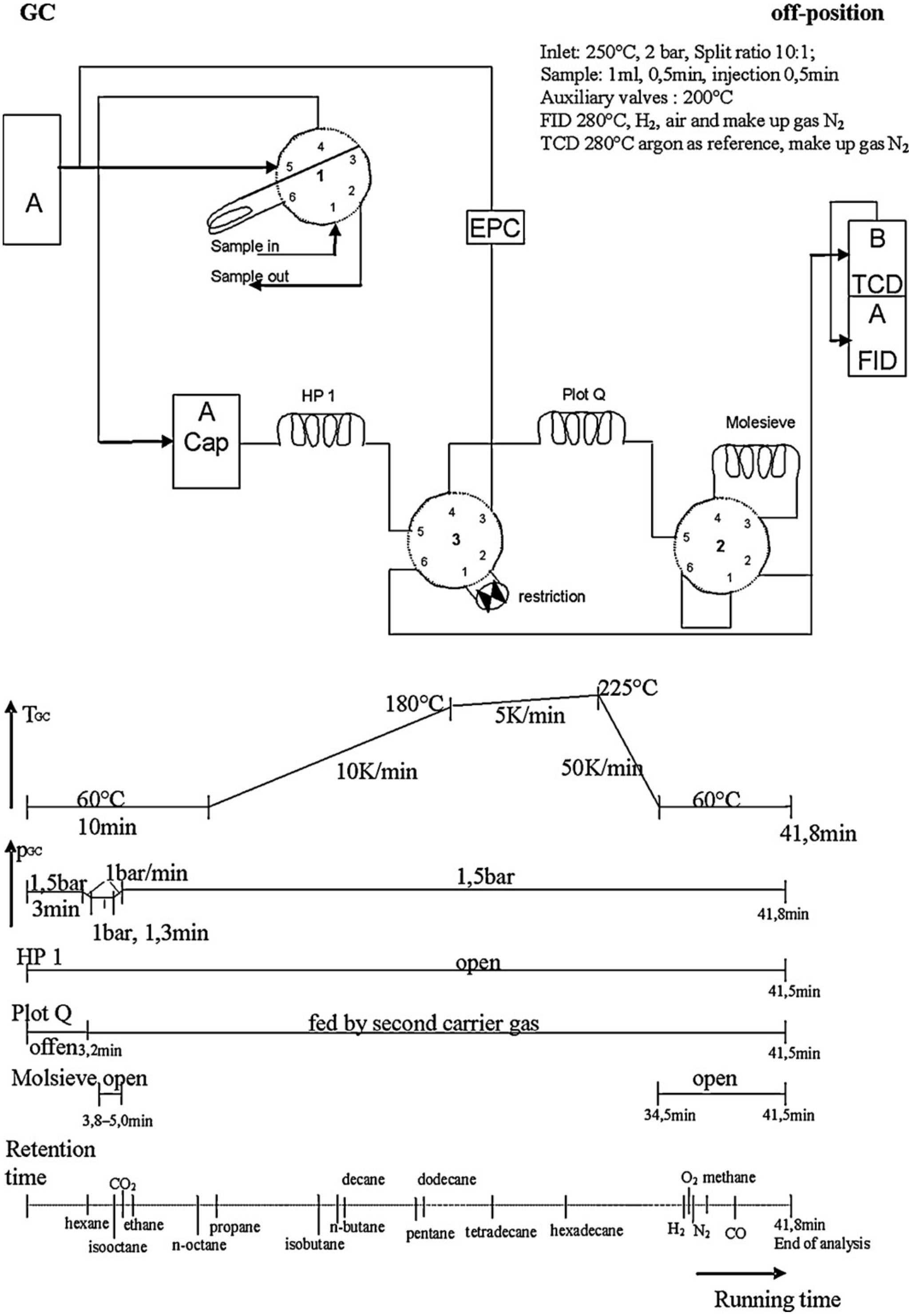

Fig. 2. Developed GC method: at the top valve system and at the bottom switching method with temperature and pressure program.

sheet and the GC method shown in Fig. 2 was developed. To preserve the PlotQ-column coating, a second carrier gas was used to purge the column during heating when no carrier gas was applied to this column. The HP1 and the PlotQ column were analysed simultaneously whereas the permanent gases trapped on the molsieve column were analysed afterwards.

2.4. Reaction conditions

Methane and propane were applied as conversion intermediates. Isooctane and hexadecane were tested, respectively, as gasoline and diesel surrogates. The reactions were carried out at ambient pressure and a temperature between 400 and 700 °C, a steam to carbon ratio of 4, and a space velocity (GHSV) between 15,000 and 25,000 h^{-1}, corresponding to a residence time between 160 and 230 ms. The experiments were conducted at steady state conditions. The reactor temperature was fixed, for example, at 400 °C and after the reforming experiment was completed, raised by 50 K. The next product gas measurement was taken after 42 min of GC run time which is enough for reaching steady state. Temperature increases were made in the same manner up to 700 °C and back from 700 to 400 °C. Catalyst regeneration to remove carbonaceous residues was performed at 750 °C in air when necessary. Subsequently the catalyst was reduced again in 2 vol% hydrogen flow. This procedure ensured to reach initial conversions and selectivities again.

To avoid deposition of carbonaceous species in general, the reaction mixture was introduced into the reactor after establishing of the desired composition.

Before catalytic testing, each catalyst was exposed to the reaction mixture for several temperature cycles to ensure stable catalyst performance. This was necessary since the catalyst improved during the first cycles under reaction conditions which was accompanied interestingly with a decrease in alumina and rhodium surface area (see next section).

3. Results and discussion

3.1. Catalyst characterisation

The catalyst characterisation primarily examines the different characteristics between the foils directly after the coating procedure with alumina and rhodium (in the following called “reference foils”) and the microchannel foils after several steam reforming experiments (in the following called “reactor foils”) as the catalyst improved during the first cycles under reaction conditions.

The *reference foil* showed a BET surface area of 71.2 m^2/g, an enhancement factor F of 146 and a dispersion of 6.1%. As depicted in Fig. 3 the coating of the reference foil is not a totally homogeneous one. Especially in the transition region from the microchannel bottom to the walls there is a curvature in the catalyst layer, i.e. higher catalyst mass in the corners.

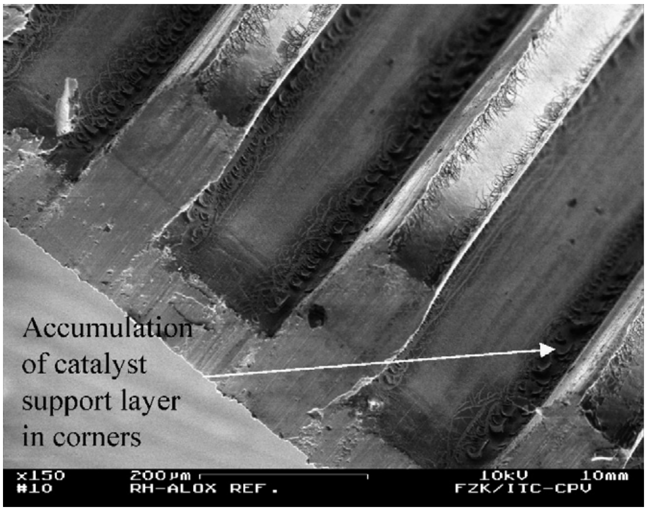

Fig. 3. SEM picture of microstructured foil directly after coating with Al_2O_3 support and rhodium impregnation.

A closer view into the microchannel with SEM (Fig. 4, left side) reveals, that in the center of each channel bottom the coating is more or less homogeneous but the transition section to the channel wall is covered with cracks in the coating.

A *reactor foil* instead shows (in Fig. 4, right side) some small and flat cracks in the middle of its channels and the material restructured and formed some kind of flaking in the transition section to the channel walls. Furthermore, the reaction foil possessed lower values for the BET surface area and the surface enhancement factor, i.e. a mean of 48.6 m^2/g and $F = 89$, respectively. The chemisorption analysis could not be performed with the *reactor foil* as the active surface area falls below the detection limit of 1 m^2.

Samples of reference and reactor foil prepared with different rhodium content exhibited the same behaviour in terms of crack formation and BET surface area and metal dispersion decrease during exposure to reaction conditions. So, this seems to be a general issue for alumina based catalysts.

To check the influence of the restructuring of the support on the catalyst more representative SEM pictures have been taken applying an inlens detector for structure information and a combination of inlens and backscattering detector for revealing material differences and highlighting the rhodium (white color). Fig. 5 shows SEM pictures taken with an inlens detector

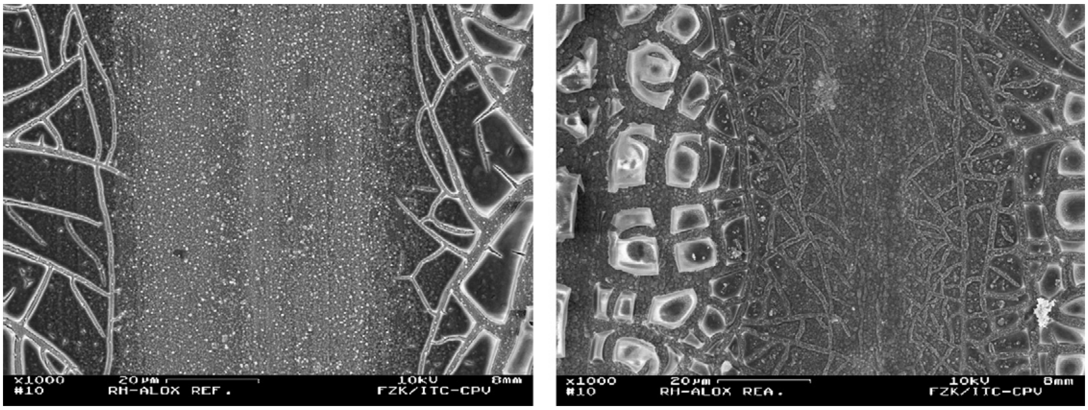

Fig. 4. Representative SEM pictures of microstructured foils: left side reference foil and right side reaction foil (Al_2O_3 based catalyst system).

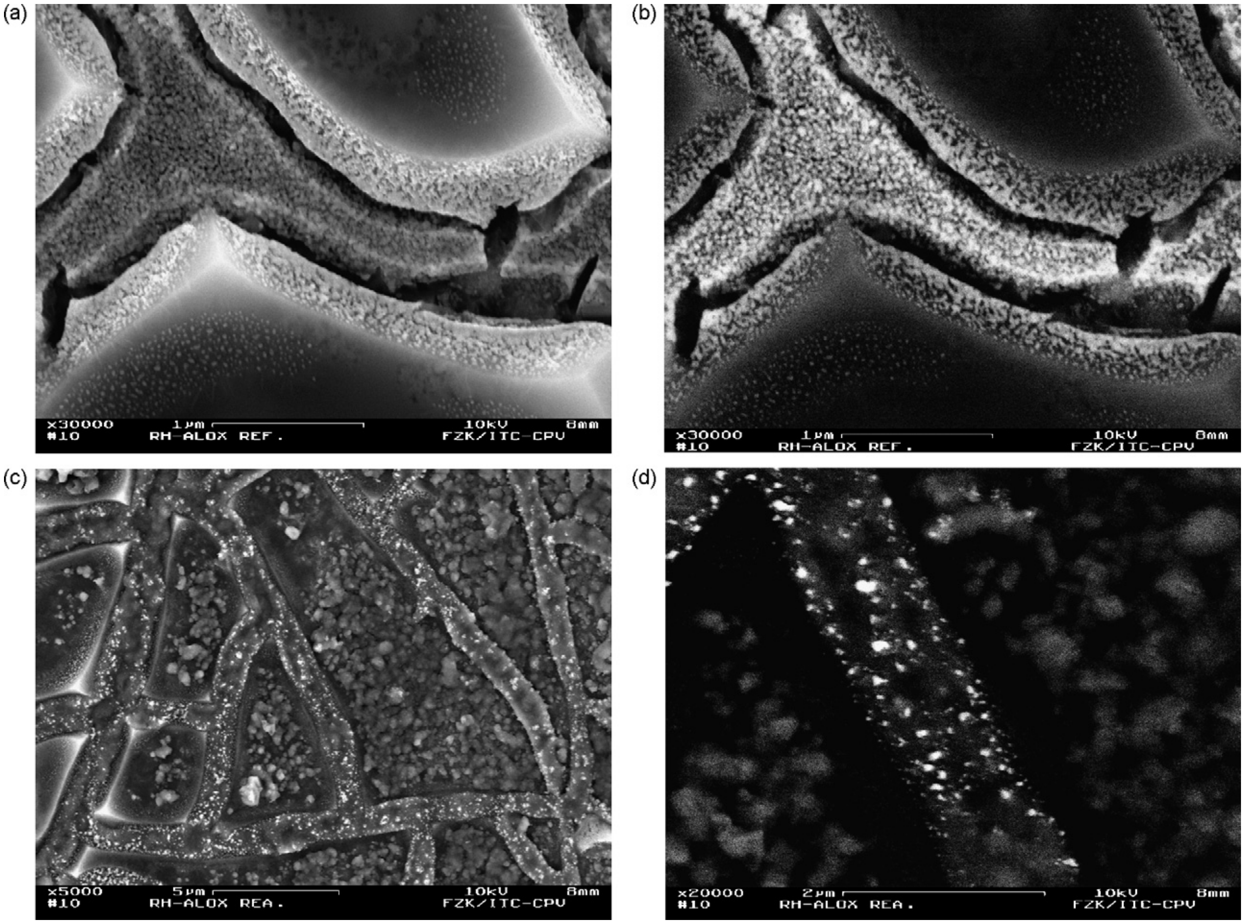

Fig. 5. SEM pictures (a) of the coating cracks on the channel bottom taken by an inlens detector, (b) by a backscatter detector on the reference foil; analogous for the reaction foil (after reaction cycles) in (c) and (d).

(Fig. 5a) and a backscatter detector (Fig. 5b) of cracks in the transition section from the bottom to the wall of a microchannel on a reference foil. From these pictures it is clear that most of the rhodium catalyst can be found in the near of these cracks. In the center of the microchannel bottom, where a homogeneous coating was reached no signal of rhodium was observable and thus is not presented here.

For the reactor foil, in contrast, rhodium can be found in the small and flat cracks in the center of the microchannels as presented in Fig. 5c and d. In the higher magnification of one section of Fig. 5c in the backscatter detector mode (Fig. 5d) it can be seen that the rhodium crystals can be found more separately located in the center of the cracks, i.e. on the microchannel bottom.

Having in mind the higher activity after reaction conditions, we can conclude that either the higher crystal size (decrease in dispersion) or the higher accessibility of the rhodium could be responsible for this effect.

3.2. Reforming results

The steam reforming experiments presented here primarily examine the reforming characteristics of different fuels, ranging from the smallest hydrocarbon molecules permissible, those that do not form soot or deactivate the catalyst, to higher hydrocarbons such as propane, isooctane, and hexadecane. Fig. 6 depicts the steam reforming results for methane, propane, and isooctane, presented as conversion of fuel (X), yield of CO_2 (Y), and the turnover frequency (TOF) in moles of fuel converted per mole of active rhodium per second. The TOF allows comparison of different catalysts and their behaviour independent of the reactor and surface area. It is defined as the velocity of the reaction measured directly at the catalyst surface, and here it represents an integral value over the whole reactor instead of the normally applied differential value. The surface area applied for the TOF calculation was determined in the fresh catalyst state (see catalyst characterization) since the surface after applying reaction conditions was no more accessible. Having in mind that initially the catalyst activity increased (see Section 2.4) during first pre-cycles of reforming but decreased in catalyst surface area (rhodium particles size increase) the absolute value of the TOF might be too low. However, for the reforming behaviour of the different fuels the values can be used for comparison within this study.

From Fig. 6 it can be seen that the endothermic steam reforming reaction depends largely on the reactor temperature and with only little hysteresis when increasing or decreasing reaction temperature (lower values of conversion, TOF and yield when decreasing reaction temperature). The highest conversion

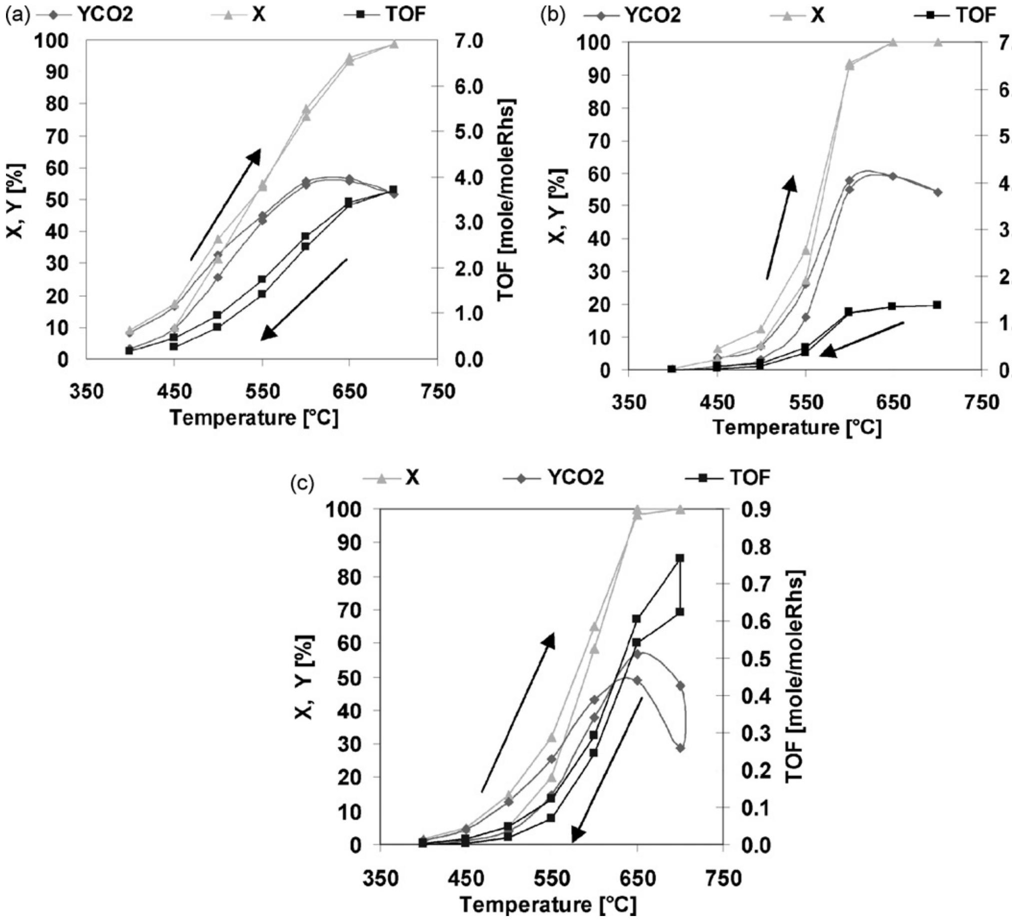

Fig. 6. Steam reforming results of (a) methane, (b) propane and (c) isooctane as a function temperature at a steam to carbon ration of 4 and a gas hourly space velocity between 15,000 and 25,000 h^{-1}. Arrows represent the hysteresis of the parameters, i.e. higher values when increasing reaction temperature and vice versa.

and fastest turnover frequency are reached at 700 °C, where the maximum error, estimated by error propagation, was less than 3% for the conversion and less than 5% for the TOF. The conversions and product gas compositions observed at 700 °C are very close to our calculations of the thermodynamic equilibrium. For example, at 400 °C the reforming of isooctane yielded a product gas composition of 0.1 vol% CO_2, 0.25 vol% H_2, 0.007% CH_4, 0.002 vol% C_2H_6, 1.02 vol% isooctane, and remaining water and nitrogen from the water excess and carrier gas. Only traces of butane were detected, and no other significant peaks or substances were observed.

At 700 °C the reforming of isooctane yielded a product gas composition of 9.7 vol% CO, 4.2 vol% CO_2, 0.6 vol% CH_4, 33.9 vol% H_2, 0.003 vol% C_4H_{10}, and remaining water and nitrogen. Again, no other substances were observed.

For every substance, methane, propane and isooctane, the conversion at 700 °C was nearly 100%. Also the yield maximum of CO_2 was always in the range of 50–60% at a temperature of 600 to 650 °C. The selectivity maximum corresponds also with thermodynamic calculations.

Real differences were observed for the maximum value of the turnover frequency. This maximum decreases for larger hydrocarbon molecules. The maximum TOF decreased from 3.7 mol/(mol s) for methane, over 1.4 mol/(mol s) for propane, down to 0.8 mol/(mol s) for isooctane. For hexadecane, a maximum value of only 0.3 mol/(mol s) was measured. For comparison with other catalytic systems, these TOF values correspond to 36–41 kg fuel converted per kg catalyst layer per hour.

Comparing also the deactivation behaviour, here only for the reforming results of hexadecane, depicted in Fig. 7, show a clear

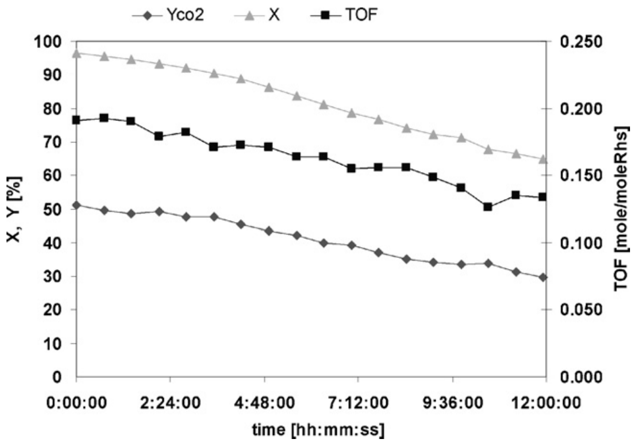

Fig. 7. Steam reforming of hexadecane at 700 °C with S/C 4 and GHSV 15,000–22,000 h^{-1}.

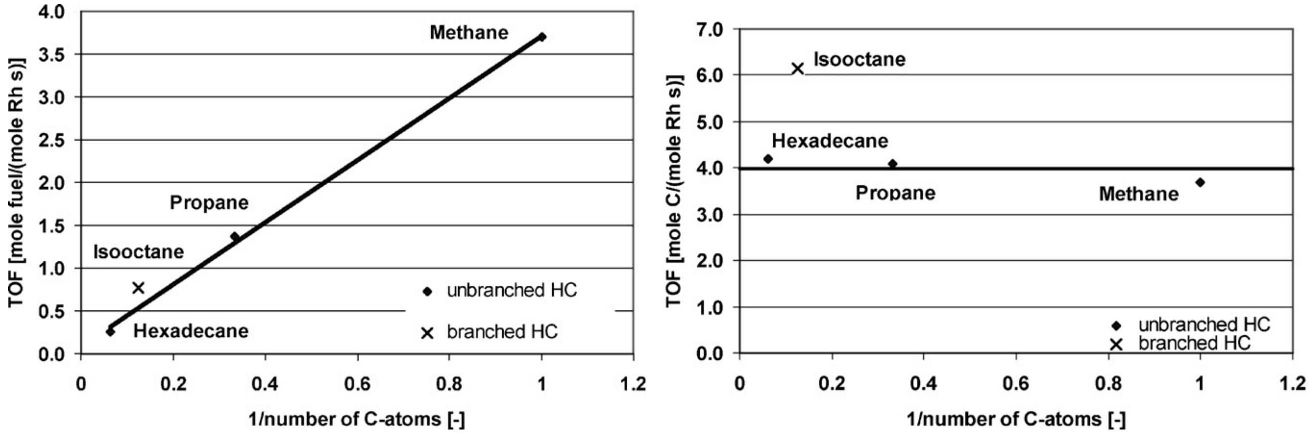

Fig. 8. Steam reforming of hydrocarbons. Turnover frequency (TOF) in dependency of the reciprocal number of C-atoms in the fuel. Left side: TOF of the whole fuel molecule. Right side: TOF of each C-atom of fuel.

decrease in the fuel conversion and in the yield of CO_2 over the experimental time was observed. During a 12-h experiment, the conversion decreased from 95% to 65%.

The decline in conversion represents a catalyst deactivation which seems to be due to soot formation as the deactivation was reversible and the catalyst activity could be completely restored after regenerating the reaction foils for 1 h in 1l/min (STP) of air at 750 °C. Optical inspection of the reaction foils also confirms the slight soot formation. Methods of soot quantification such as thermogravimetry are not possible due to the high microchannel and low soot weight as well as the oxidation of the microchannel material. Carbon dioxide formation was not detectable during the regeneration within the analytical possibilities.

The product gas from hexadecane reforming at 700 °C without catalyst deactivation consisted of 3.8 vol% CO, 4.4 vol% CO_2, 25.2 vol% H_2, 0.07 vol% CH_4, 0.03 vol% C_2H_6, 0.02 vol% $C_{16}H_{34}$, traces of pentane, hexane, and decane, as well as water and nitrogen. Again, no other significant peaks were observed.

Further comparison of the maximum turnover frequency exhibits for the unbranched alkane fuels a linear dependency on the number of C-atoms in the fuel, as shown in Fig. 8.

Branched molecules, such as isooctane, seem to be converted more easily and therefore show higher turnover frequencies, as depicted on the left side of Fig. 8. This coherence can be seen more clearly by plotting the turnover frequencies of each C-atom in the fuel feed over the reciprocal value of the number of C-atoms in the fuel, in Fig. 8 on the right side.

Since the experiments were performed at a fixed steam flow rate and a fixed steam to carbon ratio the partial pressure of the hydrocarbon varies with the number of C-atoms of the hydrocarbon in our experiments. Rostrup-Nielsen [6] performed experiments in the same manner and therefore proposed that the turnover frequencies should be corrected by the actual partial pressures of hydrocarbons. This correction results in the statement that normal paraffins become more active with increasing number of carbon atoms. Actually, these correction calculations include the assumption of first order kinetics and no product inhibiting effect. The reaction system of Rostrup-Nielsen utilised a nickel catalyst. As the reaction kinetics are not known for the system used in our study, which includes rhodium on alumina support furthermore exhibiting a conversion decline at hydrogen co-feed in preliminary results (not shown here), this correction is surely not applicable to our conditions.

Comparing our study with those of Wang and Gorte [7] we found that they also presented uncorrected results of yield, conversion, and/or turnover frequencies. There methane is the least active *n*-alkane molecule, and higher *n*-alkanes are mostly more reactive than lower *n*-alkanes. However, also Wang used a different catalyst system, i.e. Pd/Ce which makes the comparison difficult, although the value of the TOF permits to compare reforming performance without considering the reactor dimensions or design.

Neglecting the catalyst dependence it seems that our results presented above are in accordance to Rostrup-Nielsen statements that isoparaffins are known to be more active in steam reforming than *n*-paraffins [6]. A further literature comparison shows that it is at least commonly accepted that aromatics are, in general, less active at steam reforming than paraffins [7–9].

4. Conclusions

The steam reforming experiments with diesel surrogate and conversion intermediates performed well on the catalyst system rhodium on alumina deposited in microchannels.

To ensure stable performance of the catalyst system which manifests in higher conversion activity than as in the freshly prepared catalyst state, each catalyst was exposed to the reaction mixture for several temperature cycles. The catalyst characterisation by surface area measurements and SEM pictures, revealed a decrease in the BET surface area from 72 down to 49 m^2/g, a decrease in metal dispersion (below detection limit after exposure to reaction conditions) and a restructuring of the support and the rhodium coating on the channel bottom during this exposure. So, the initial increase in steam reforming activity can be either attributed to the higher crystal size or to the higher accessibility of the rhodium. The latter was seen from the appearance of rhodium in the cracks formed after exposure to reaction conditions.

At a reaction temperature of 700 °C almost 100% conversion could be achieved for methane, propane and isooctane. The model substance for diesel fuel, hexadecane, was converted up to 96%, but showed rapid catalyst deactivation within 12 h. This deactivation was most likely due to soot formation and thus reversible within one hour. Comparing the measured turnover frequencies of the different feeds reached at 700 °C shows for the TOF a linear dependency of the reciprocal value of the number of C-atoms in the fuel for the unbranched molecules, decreasing from methane to lower values of the maximum TOF for hexadecane. Branched molecules like isooctane seem to be more active and show a larger turnover frequency which is in accordance with the experiments of other authors. We additionally conclude that C−C bonds seem to be converted in an adsorbed state of both C due to the reciprocal dependency and due to negligible byproduct formation. Moreover, the negligible byproduct formation and the reciprocal dependency lead to the assumption that most of the conversion in the microchannels is performed on the catalyst surface and not in the gas phase.

Ongoing work examines in more detail diesel fuel reforming by considering individual contributions of a greater number of diesel fuel constituents. Process parameter optimisation and strategies for improving the catalyst operating time are also important to the investigation. These experimental results in consideration with start up and load changing behaviour will lead to the design and construction of an optimised microchannel reformer for diesel fuel. This system reactor will then take into account the advantages of micro reactors such as replacing the electrical heating by exothermic combustion channels adjacent to the endothermic reformer channels.

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