Investigations on Steam Reforming Catalysts for Diesel Fuel

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Abstract

Fuel cells can be applied as highly efficient auxiliary power units when being supplied with hydrogen. Since there is no adequate hydrogen infrastructure available yet, liquid fuels like Diesel can serve as a hydrogen source when it is converted into a hydrogen-rich gas in a reforming process fuel conversion by steam reforming (SR) promises the highest hydrogen yield in comparison to autothermal reforming (ATR) or catalytic partial oxidation (CPO). In the presented work several SR catalysts were tested at 750 °C and a steam to carbon ratio of 4, using a Diesel reference fuel with a sulphur content of $\xi_s < 10$ ppm. Steam reforming was studied for varying Gas Hourly Space Velocities (GHSV) with respect to the hydrogen yield. In addition, studies of catalyst deactivation in the presence of sulphur and the catalysts' ability to regenerate by carbon combustion with air were completed. Some catalysts show promising results, while we identify one catalyst that has a high potential for a continuous Diesel SR application. Closing the presentation, we discuss the reproducibility of the results, and we give recommendations for further investigations.

1   Introduction

Fuel cells (FC) are highly efficient energy converters that can be applied as stationary or mobile auxiliary power units (APU) when being supplied with hydrogen. The fact that there is no adequate hydrogen infrastructure available yet drives alternative approaches to supply FC. In order to facilitate a breakthrough of the technology, a promising approach is the use of hydrocarbons as a hydrogen source. In particular for mobile applications, liquid fossil fuels like Diesel are suitable due to their high energy density, their easy storage and their already existing distribution infrastructure.

To generate hydrogen from Diesel, reforming processes like steam reforming (SR), autothermal reforming (ATR) or catalytic partial oxidiation (CPO) have to be applied. In comparison to ATR and CPO, SR promises a higher hydrogen yield generating hydrogen from hydrocarbons and steam, based on catalytic reactions. However, steam reforming Diesel is challenging because of its complex composition of aromatic and aliphatic hydrocarbons and its sulphur content. Sulphur is a catalyst poison blocking the catalyst's active surface. In the same way the catalyst is deactivated by carbon deposits, formed during the reforming process. To overcome catalyst deactivation and to achieve long-term durability for Diesel SR, suitable catalysts have to be found.

In recent years, there have been efforts to develop sulphur-tolerant catalysts that are capable to convert Diesel and fossil fuels of similar compositions at high conversion rates. Kataria et al. performed investigations on steam reforming of jet fuel with sulphur contents of 100 ppm.

They observed a dramatic decrease in catalyst activity with time in comparison to processing a sulphur free fuel. They also found that the sulphur content promoted carbon formation [3]. Steam reformer for light fuel oil and Diesel were investigated by several authors [1, 4, 6]. Reformer tests were conducted with a sulphur free reference fuel and desulphurised Diesel. The results show that lower temperatures as well as increased flow rates result in lower conversion rates [1, 2]. The reforming of desulphurised Diesel with sulphur contents <1 ppm already shows a noticeable catalyst deactivation [5]. Thormann carried out steam reforming experiments on synthetic Diesel and conventional Diesel with sulphur contents <10 ppm using rhodium catalysts. He found that catalyst deactivation is significant but reversible [4].

The results of prior research show the necessity to further develop SR catalysts for sulphur containing liquid fuels. In order to use liquid fuels as a hydrogen source for FC, new catalysts have to be found that offer high fuel conversion rates, low deactivation tendency and the ability to regenerate from deactivation.

The presented work describes the tests of 9 noble metal catalyst samples of different formulations for Diesel SR. Diesel reference fuel with a sulphur content of 6 ppm was reformed in order to study the catalyst performance at different Gas Hourly Space Velocities (GHSV) and the catalyst deactivation. Considering long-term durability, the regeneration ability was investigated, observing the product gas concentrations after the combustion of carbon deposits with air.

2   Materials and Methods

For the catalyst tests, Diesel reference fuel and de-ionised water with a conductivity lower 10 µS/cm were used. The fuel composition was determined to comprise of the fractions as described in Table 1.

Table 1:   Fractions of the used Diesel reference fuel.

Content	Test method	Value	Unit
Alkane, Naphthene		72,5	% by weight
Polycyclic aromatic hydrocarbons	DIN EN 12916	3,3	% by weight
Mono-aromatic		20,9	% by weight
Di-aromatic		3,2	% by weight
Tri-aromatic		0,1	% by weight
sulphur	DIN EN ISO 20884	6	mg/kg

The catalyst tests were completed on the test rig as shown in Figure 1. The rig comprised of the five main sections: dosing, mixture preparation, mixture conditioning, steam reforming and analysis.
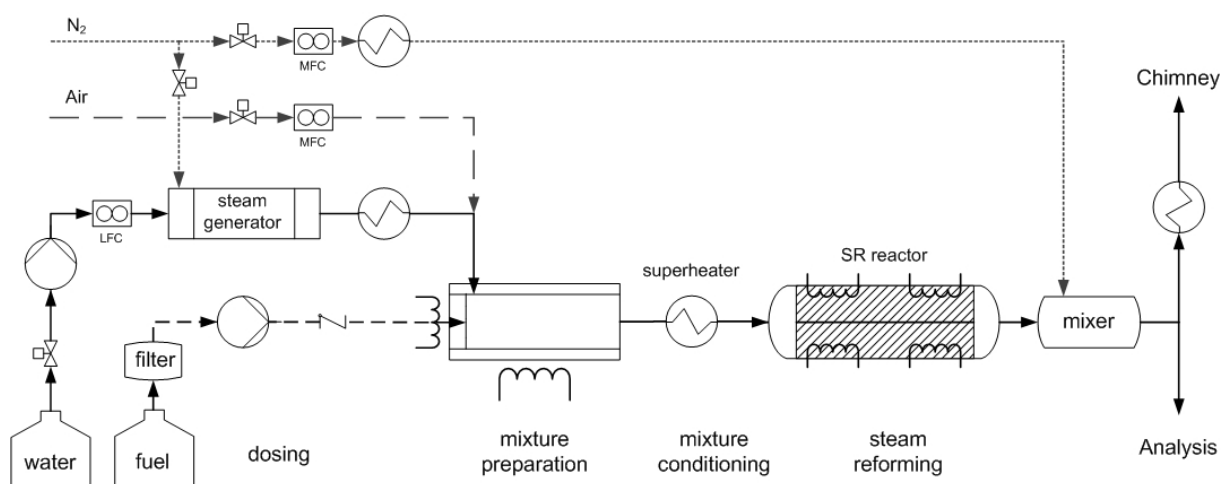
Figure 1:   Test rig for steam reforming studies.

For dosing Diesel a dosing pump was employed, pumping the fuel into the mixture preparation device to vaporise on a heated porous surface. Water was dosed and vaporised in a controlled steam generator. The generated steam was superheated and led into the mixture preparation device to mix with the Diesel vapour at a temperature of approximately 450 °C. In the mixture conditioning zone the Diesel-steam-mixture heated up to provide consistent inlet temperatures of 750 °C for the SR reactor. The reactor consisted of a single channel of catalytically coated plates embedded into a heated body to achieve isothermal conditions for the reforming reactions.

Steam reforming was studied at 750 °C, and a steam to carbon ratio (S/C) of 4 was applied. Starting with an initial fuel feed corresponding to a thermal power input of 0.75 kW$_{th}$, the power input was increased stepwise to 1.00 kW$_{th}$ and 1.25 kW$_{th}$.

The resulting educt flows corresponded to the GHSVs of 45,000 h^{-1}, 60,000 h^{-1} and 75,000 h^{-1}, relating the GHSV to the channel volume. The product gas was continuously analysed over the test period, measuring hydrogen (H$_2$), carbon monoxide (CO), carbon dioxide (CO$_2$) and methane (CH$_4$) concentrations with a Rosemount NGA 2000 analyser. Unconverted hydrocarbons were analysed with a Rosemount Thermo-FID to determine the fuel conversion rate. Due to technical FID limitations, the product gas was diluted to H$_2$ concentrations lower 10 % V/V with nitrogen. FID measurements were taken in five reading points over a test period (cp. Figure 2) when steady-state reactor temperatures were reached. Steady-state was considered when temperature deviation from set temperatures was lower 5 K at the reactor inlet and outlet. After reading point 3, the process was run at a constant fuel feed equivalent to 1.25 kW$_{th}$ to observe the deactivation of the catalyst. Then, the reactor was flushed with nitrogen to initiate the regeneration process, using air for the combustion of carbon deposits. To evaluate the regeneration ability of the catalyst the initial fuel feed was set for another measurement.

3   Results and Discussion

In our study 9 noble metal catalyst samples (A1 to A9) were investigated. in order to show reproducibility of the results, catalyst A4 was of the same formulation as A3 and A6 was of

the same formulation as A5. As an example, Figure 2 shows the results of the test with catalyst A7. We obtain an initial H_2 concentration of more than 68 % before it falls due to the fuel feed increase resulting in higher GHSVs and therefore lower conversion rate. The increased GHSV also causes dropping CO_2 concentrations and rising CO concentrations revealing a reduction of the shift reaction. In the beginning of the degradation study (cp. Figure 2: reading point 3 to 4) we still find 63 % H_2 in the product gas. The catalyst activity steadily drops within the 3 hour study duration, but can partially be recovered after the regeneration with air. The CO_2 peak in the regeneration indicates the combustion of carbon deposits, and therefore suggests that deactivation from carbon formation is reversible. Evidently, we obtain a significant higher H_2 yield after the regeneration. This result is consistent to prior studies that suggest that deactivation is primarily from carbon formation [2]. The H_2 yield, however, does not reach the initial value, suggesting that the regeneration duration is insufficient to regenerate the catalyst from sulphur deactivation.

Figure 3 describes the catalyst performances for three fuel feeds in terms of the achieved H_2 yields. At the the initial fuel feed of 0.75 kW, accordant to a GHSV of 45,000 h^{-1}, the hydrogen yields are in a close range of a minimum of 64 % (A3) and a maximum of 68 % (A2). However, the catalysts respond differently to increased fuel feeds and thereby higher GHSVs. The performances of catalysts A4 and A6 significantly drop for a fuel feed of 1.25 kW accordant to a GHSV of 75,000 h^{-1}. Catalyst A7, in contrast, is the least sensitive to higher GHSVs. The best hydrogen yield at the highest fuel feed is obtained with catalyst A2.
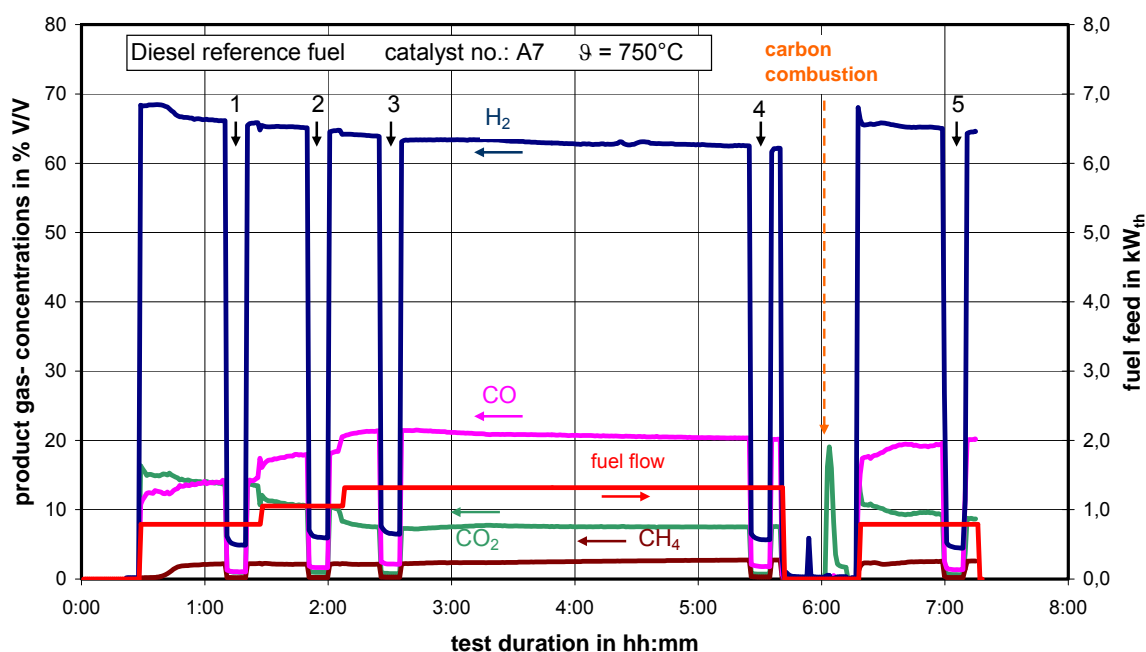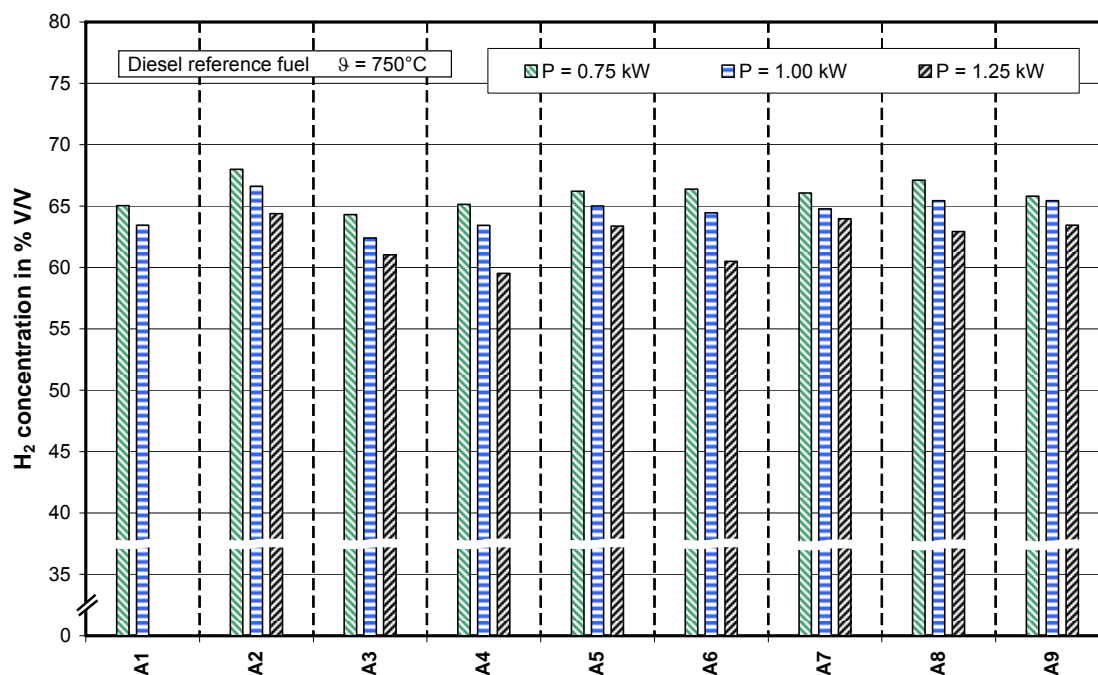

Figure 2:   Product gas-concentrations achieved with catalyst A7.

Figure 3: **H2 yield of all catalysts for the investigated fuel feeds.**

The results of the catalyst deactivation study are shown in Figure 4 by means of the degradation rate D. The degradation rate is calculated from the concentrations measured at reading points 3 and 4, the GHSV and the time between the reading points.

$$D = \frac{c_3 - c_4}{c_3 \quad \Delta t_{3,4} \quad GHSV}$$

The degradation rate is described for fuel conversion, H_2 concentration, CO_2 concentration and CO concentration within which the main focus has to be on the degradation of fuel conversion due to the applicability for Diesel reformers. We find that degradation characteristics in fuel conversion vary significantly among the catalysts. However, as a result of the necessary dilution for the FID measurement, the value for fuel conversion is the most sensitive to measurement errors. We, therefore, concentrate on degradation of H_2 concentrations to evaluate the catalysts.

Catalysts A1, A3 and A9 show good degradation characteristics for all gas concentrations while catalyst A7 seems to be exceptionally suitable for Diesel SR. Catalysts A2 and A5 can be considered unsuitable for a Diesel reformer due to their high degradation rates. High degradation in CO_2 concentrations along with a considerable low degradation for CO indicates that the shift reaction is being constrained due to the catalyst deactivation, as can be observed for A3. In contrast, the shift reaction seems to be enhanced for catalyst A8.
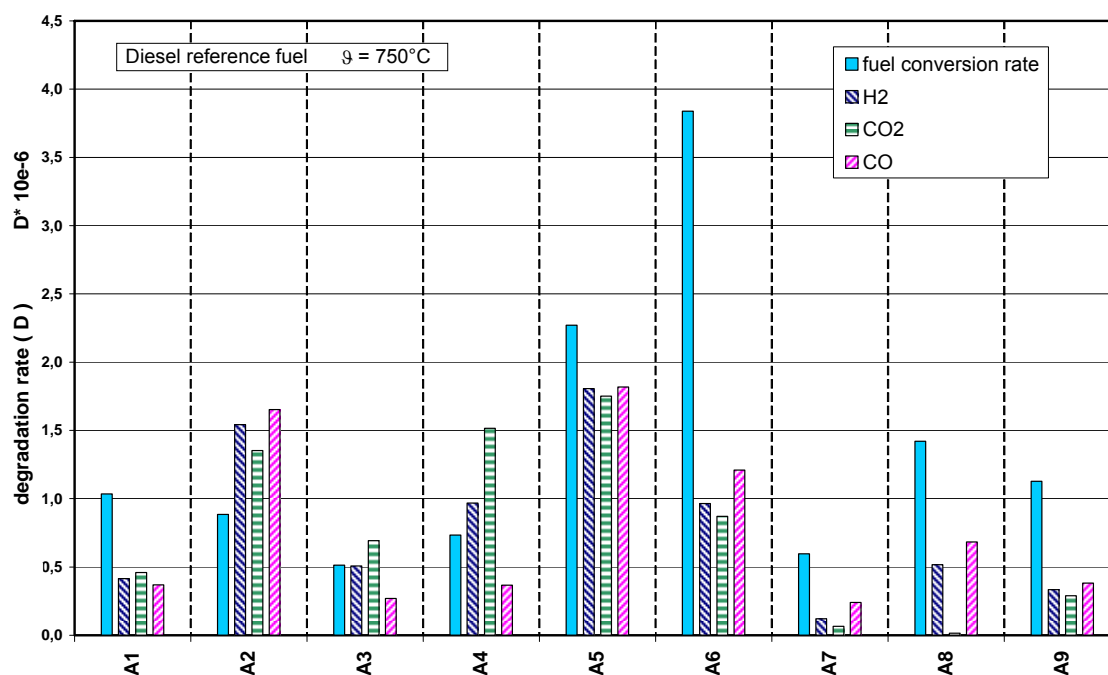
Figure 4:   Results of the deactivation study.

The regeneration ability of the catalysts, described in Figure 5, is evaluated by the comparison of initial product gas concentrations and final concentrations after regeneration. For catalysts A6 and A9 we find nearly initial gas concentrations indicating that quasi full regeneration of the catalysts is possible. However, in reproducing the test results of catalyst A5 with A6, we had to stop the degradation study due to dramatic catalyst deactivation. Hence, there was less time for sulphur to deactivate the catalyst.

For the rest of the catalysts no satisfying regeneration was achieved. Additionally, we observe a decreased shifting ability for catalysts A5, A7 and A8, revealed by higher CO concentrations along with lower CO_2 concentrations.

In reproducing the test results, we find good reproducibility for catalyst A3 (cp. catalyst A4). Comparing the results for A5 and A6 we observe major discrepancies. We suppose that they may occur due to varying test durations and varying times for the reading points. Steady-state temperatures, being the precondition for measurements, were reached at different times. Furthermore, we had to advance regeneration due to the high catalyst deactivation. We recommend that further investigations are being conducted using an automated testing procedure with consistent test durations.

Summarising the results, we find that no catalyst in particular comprehends optimum characteristics in every aspect. Catalyst A7, however, shows the highest potential for an application in a continuous Diesel steam reforming process.
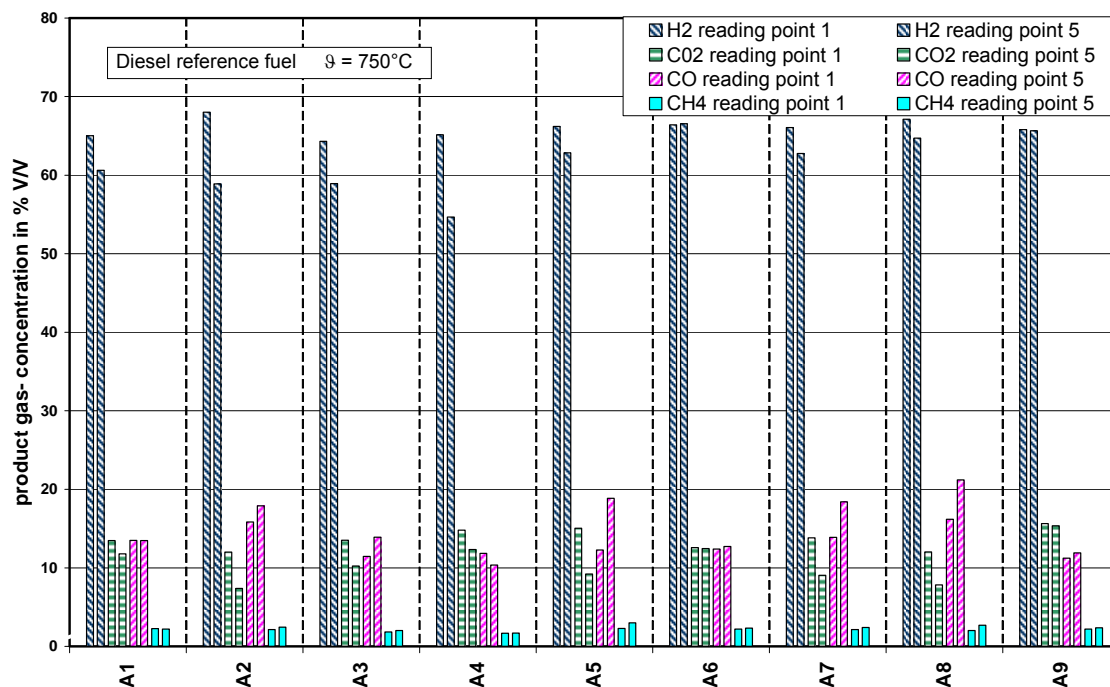
Figure 5:   Regeneration ability of the catalysts.

4   Significance

Due to their high efficiencies, fuel cell systems are very attractive alternative to existing electric power generators applied as APUs. In particular for mobile applications, FC systems based on liquid fuels are promising since there are no storage or handling issues in contrast to the usage of pure hydrogen. Diesel is a liquid fuel that is already in use for heavy-duty and conventional vehicles, and hence has an existing distribution infrastructure. Steam reforming Diesel in order to supply FC with hydrogen, however, is challenging because of its sulphur content that deactivates the SR catalyst. Several SR catalyst were identified that showed promising characteristics in the presence of sulphur. One catalyst in particular showed high potential for a Diesel steam reformer. To verify the results and to improve reproducibility, an automated test procedure has to be applied in further studies.

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