Hydrogen production from bio-fuels using precious metal catalysts

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Key words: catalyst activity; catalyst characterization; autothermal reforming; commercial diesel fuel; fuel cells

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Abstract

Fuel cell systems with integrated autothermal reforming unit require active and robust catalysts for H_2 production. Thus, an experimental screening of catalysts for autothermal reforming of commercial bio-diesel fuel was performed. Catalysts consisted of a monolithic cordierite substrate, an oxide support (γ-Al_2O_3) and Pt, Ru, Ni, PtRh and PtRu as active phase. Experiments were run by widely varying the O_2/C and H_2O/C molar ratios at different gas hourly space velocities. Fresh and aged catalysts were characterized by temperature programmed methods and thermogravimetry to find correlations with catalytic activity and stability.

Introduction

According to the current policies scenario, by 2030 the global CO_2 emissions will be more than 50% higher than today. In addition, the world population is supposed to grow to more than 9 billion of people in 2050. As a consequence, the energy demand strongly increases, especially driven by China and India. The Institute of Energy and Climate Research (IEK-3) at Forschungszentrum Jülich has been developing a two-step approach to contribute to facing these environmental problems. On the one hand, efficient fuel cell systems based on the autothermal reforming of diesel fuels have been developed, which can be used as auxiliary power units for efficient on-board power supply in aircraft or long-haul trucks, for example. On the other hand, a renewable Bio-To-Liquid (BTL) fuel is used as feedstock for these systems.

Biodiesel fuel synthesized by hydro-treating of triglycerides

Transesterification is one of the most important routes for the production of bio-fuels [1-3]. During this process, triglycerides from vegetable oil or animal and plant fats are converted with alcohol molecules (methanol or ethanol) yielding mono-alkyl esters and glycerol. The mono-alky ester molecules then make up the bio-diesel. Another option for the production of bio-diesel is hydro-treating. This process

can be run in existing petroleum refineries [4]. Figure 1 shows a simplified scheme for the conversion of triglycerides contained in Jatropha oil, algae oil or plant and animal fats to straight-chain and branched alkanes [4]. In the first two steps of this reaction scheme, the triglyceride molecule is hydrogenated and split into a number of intermediates which can be monoglycerides, diglycerides and carboxylic acids. These intermediates are then converted into alkanes on three different routes: decarboxylation, decarbonylation and a combination of hydrogenation with dehydration. Reaction equations (1)-(3) show exemplarily the different routes for alkane production starting from carboxylic acids. Decarboxylation involves converting a carboxylic acid into a methyl group and CO_2 as shown in equation (1). CO is produced by decarbonylation where the carboxylic carbon is reduced by hydrogen to yield a methyl group, CO and water appear as side products, as shown by equation (2). During the combination of hydrogenation with dehydration the carboxylic acid reacts with hydrogen to produce an alkane and water as shown by the third equation [4].

$$R\text{-}CH_2\text{-}COOH \qquad \longleftrightarrow \qquad R\text{-}CH_3 + CO_2 \qquad\qquad (1)$$

$$R\text{-}CH_2\text{-}COOH \quad + H_2 \qquad \longleftrightarrow \qquad R\text{-}CH_3 + CO + H_2O \qquad\qquad (2)$$

$$R\text{-}CH_2\text{-}COOH \quad + 3\,H_2 \qquad \longleftrightarrow \qquad R\text{-}CH_2\text{-}CH_3 + 2\,H_2O \qquad\qquad (3)$$

For the investigations in this work, so-called NExBTL diesel fuel produced by the Finnish company Neste was used as fuel for the autothermal reforming reactor. NExBTL diesel fuel has a sulfur mass proportion of less than 1 ppm and a fraction of aromatics far lower than 1 vol%.
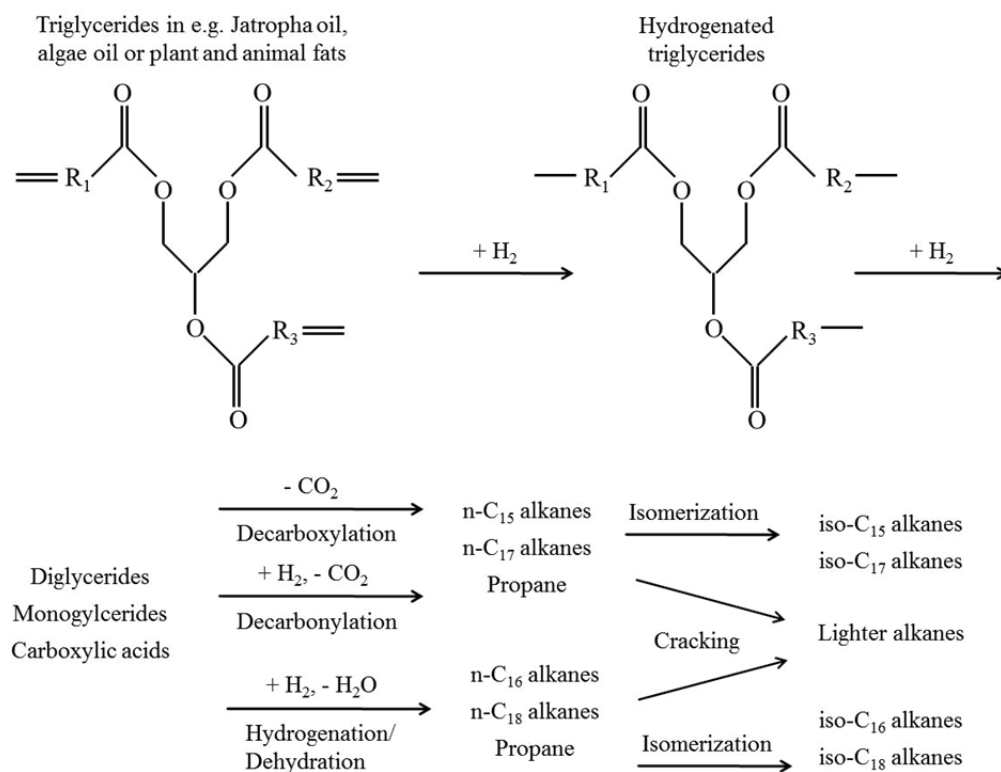

Figure 1   Simplified scheme for the conversion of triglycerides contained in in Jatropha oil, algae oil or plant and animal fats to straight-chain and branched alkanes [4]

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Catalyst preparation

The catalysts were synthesized in mass fractions related to the cordierite substrates, whereby for the oxide support and the active metal phase approx. 10 wt.% and 1 wt.%, respectively, were obtained. Each value referred to the total mass of the catalyst. The synthesis of the support γ-Al_2O_3 was identical to that described in previous work [5] except for the temperature, at which the impregnated cordierite substrate was dried after impregnation. This temperature was decreased from 110 °C to 80 °C in order to reach a more homogeneous coating of the support on the substrate. For the synthesis of the bimetallic catalyst PtRu/γ-Al_2O_3 with 0.5 wt.% Pt and 0.5 wt.% Ru, the cordierite substrate, which was already coated with γ-Al_2O_3, was at first impregnated with a precursor solution of $Ru(O_2C_5H_7)_3$ (tris(acetylacetonato)ruthenium (III), dissolved in tetrahydrofurane). This impregnation step was performed twice from the top and the bottom side of the cylindrical substrate, respectively, to ensure a homogeneous coating. The substrate was then dried at 60 °C for 2 hours and calcined at 700 °C for 1 hour. In a second step, this substrate was impregnated with a precursor solution of $[Pt(NH_3)_4](NO_3)_2$ (tetraammineplatinum (II) nitrate). Then, the substrate was dried at 80 °C for 2 hours and calcined at 700 °C for 1 hour. For the synthesis of the bimetallic catalyst PtRh/γ-Al_2O_3 with 0.5 wt.% Pt and 0.5 wt.% Rh, the γ-Al_2O_3 coated cordierite substrate was at first impregnated with a precursor solution of $Rh(NO_3)_3$, then dried at 80 °C for 2 hours and calcined at 700 °C for 1 hour. Again, the impregnation step was performed twice from the top and the bottom side of the cylindrical substrate, respectively, to ensure a homogeneous coating. In a second step, the substrate was impregnated with a precursor solution of $[Pt(NH_3)_4](NO_3)_2$ (tetraammineplatinum (II) nitrate), dried at 80 °C for 2 hours and calcined at 700 °C for 1 hour. The preparation of the monometallic catalyst Pt/γ-Al_2O_3 with 1.0 wt.% was performed by impregnation of the γ-Al_2O_3 coated cordierite substrate with a precursor solution of $[Pt(NH_3)_4](NO_3)_2$ (tetraammineplatinum (II) nitrate). The substrate was then dried at 80 °C for 2 hours and calcined at 700 °C for 1 hour.

Analogously, the monometallic catalyst Ru/γ-Al_2O_3 with 1.0 wt.% was prepared by impregnating the γ-Al_2O_3 coated cordierite substrate with a precursor solution of $Ru(O_2C_5H_7)_3$ (tris(acetylacetonato)ruthenium (III), dissolved in tetrahydrofurane). The substrate was then dried at 80 °C for 2 hours and calcined at 700 °C for 1 hour. The catalyst Ni/γ-Al_2O_3 was synthesized using a $Ni(NO_3)_3 * 6\ H_2O$ precursor solution. The γ-Al_2O_3 coated cordierite substrate was impregnated with this solution, dried at 80 °C for 2 hours and calcined at 700 °C for 1 hour.

Results and discussion

In the above mentioned previous work by our group [5], it was demonstrated that among the investigated samples Rh/γ-Al_2O_3, Rh/La-Al_2O_3, Rh/CeO_2, Rh/Gd-CeO_2, Rh/ZrO_2 and Rh/Y-ZrO_2 the catalyst Rh/γ-Al_2O_3 had the highest initial catalytic activity and showed the lowest catalytic deactivation in the course of the applied evaluation pattern under rough reaction conditions. For that reason, it was decided to choose γ-Al_2O_3 as catalyst support for the experiments of this contribution. In this respect, Figure 2 shows H_2 concentrations of catalysts Pt/γ-Al_2O_3, Ru/γ-Al_2O_3, Ni/γ-Al_2O_3, PtRh/γ-Al_2O_3 and PtRu/γ-Al_2O_3 as a function of the H_2O/C molar ratio at an O_2/C molar ratio of 0.47 and different GHSVs. NExBTL diesel fuel was used. For means of comparison, the corresponding trend of the H_2

concentration of catalysts Rh/γ-Al$_2$O$_3$ from previous work taken under identical reaction conditions was added to Figure 2. The first sequence was started at a H$_2$O/C molar ratio of 2.1 and a GHSV of 59,000 h^{-1}. That means, Figure 2 has to be interpreted from right to left.
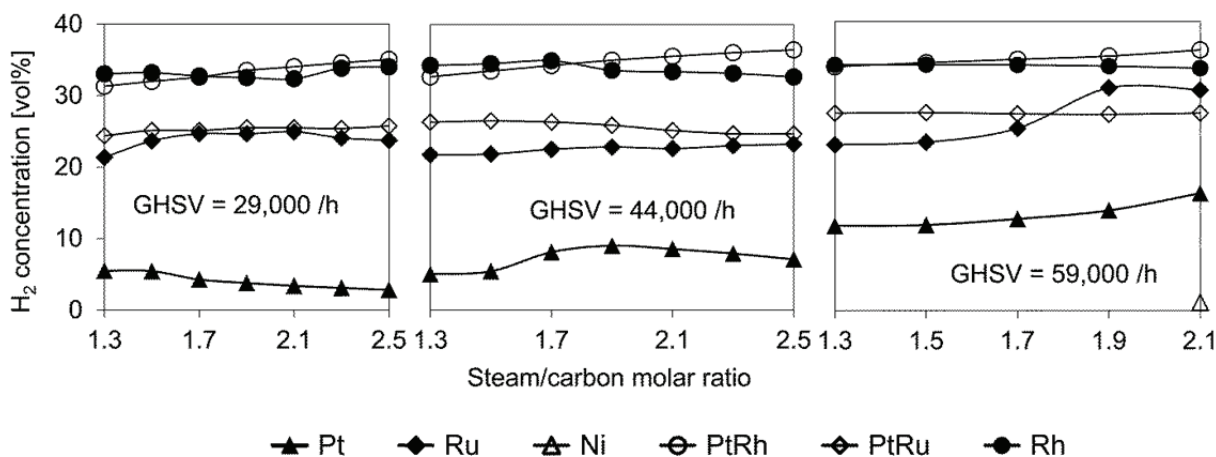

Figure 2   H$_2$ concentration on all six catalysts as a function of the H$_2$O/C molar ratio, O$_2$/C molar ratio = 0.47, at different mean GHSVs, NExBTL diesel fuel

Figure 2 shows a very low H$_2$ concentration in the range of only 3 vol% for the catalyst Ni/γ-Al$_2$O$_3$ at the beginning of the first sequence (H$_2$O/C molar ratio of 2.1). The experimental evaluation of this catalyst had to be stopped after this first experiment. Otherwise, the large residual mass stream of unconverted hydrocarbons in NExBTL diesel fuel would have severely contaminated and destroyed many components of the test rig downstream the catalytic test reactor including the gas analytical system. Also the sample Pt/γ-Al$_2$O$_3$ showed comparatively low H$_2$ concentrations between 16 and 11 vol% during the first sequence in Figure 2. The values of catalyst Ru/γ-Al$_2$O$_3$ started at a higher level of approx. 31 vol% but then decreased with decreasing H$_2$O/C molar ratio to approx. 23 vol%. The bimetallic catalyst PtRu/γ-Al$_2$O$_3$ revealed very stable H$_2$ concentrations of approx. 27 vol% independent of the H$_2$O/C molar ratio. Thus, the addition of Ru to the Pt-based catalyst had a very positive effect on the catalytic activity. The bimetallic sample PtRh/γ-Al$_2$O$_3$ and the reference catalyst Rh/γ-Al$_2$O$_3$ showed highest H$_2$ concentrations ranging from 36 to 34 vol% for the bimetallic catalyst and from 33.5 to 34 vol% for the reference catalyst from previous work.

Figure 2 in the middle and on the left show the results of the second and third experimental sequence with respect to H$_2$ concentrations of the five investigated catalysts and the reference sample. The catalysts were not replaced between the first and second or between the second and third sequence. This means that the series of sequences run with each catalyst can be considered an accelerated aging experiment. It can be seen that during sequences 2 and 3 the H$_2$ concentrations of the catalyst Pt/γ-Al$_2$O$_3$ further decreased to values between 9 vol% and only 3 vol%. An additional deactivation of this catalyst for autothermal reforming occurred. As a consequence of the deactivation step from the first sequence, the H$_2$ concentrations of the monometallic catalyst Ru/γ-Al$_2$O$_3$ were always lower than those of the bimetallic sample PtRu/γ-Al$_2$O$_3$ during the second and third sequence. At a GHSV of 44,000 h^{-1}, they were almost constant at 22 – 23 vol% and thus in the same order magnitude as after

the deactivation step in the first sequence. During the third sequence at a GHSV of 29,000 h^{-1}, the values for the H$_2$ concentration of Ru/γ-Al$_2$O$_3$ slightly increased to 25 vol% at most favorable H$_2$O/C molar ratios between 2.1 and 1.7. Obviously, the lower residence time during the third sequence had a positive effect on the catalytic activity of Ru/γ-Al$_2$O$_3$. As mentioned above the H$_2$ concentrations of the bimetallic sample PtRu/γ-Al$_2$O$_3$ were always slightly higher than those of Ru/γ-Al$_2$O$_3$ during the second and third sequence. The values for PtRu/γ-Al$_2$O$_3$ were quite stable between 25 and 26 vol% thus showing no sign of deactivation. However, it can be concluded from the first three sequences that both catalysts, Ru/γ-Al$_2$O$_3$ and PtRu/γ-Al$_2$O$_3$, were also not suitable for efficient autothermal reforming of BTL diesel fuel. The observed H$_2$ concentrations were simply too low compared to those given in the literature. This would lead to poor H$_2$-productivity of the reforming step within a fuel cell system and thus also significantly reduce the overall efficiency of the whole fuel cell system. Also during the second and third sequence the H$_2$ concentrations of the bimetallic catalyst PtRh/γ-Al$_2$O$_3$ were highest among the investigated samples and varied between 34 and 36 vol% at most favorable H$_2$O/C molar ratios between 2.3 and 1.9. Under these reaction conditions these values were even higher than those of the reference catalyst Rh/γ-Al$_2$O$_3$, which was considered suitable for autothermal reforming of diesel fuels in previous work [5]. So, from the first three sequences with widely varying H$_2$O/C molar ratios it can be concluded that the bimetallic catalyst PtRh/γ-Al$_2$O$_3$ from this work is promising for the autothermal reforming of BTL diesel fuel. It showed a high initial catalytic activity and no detectable signs of deactivation.
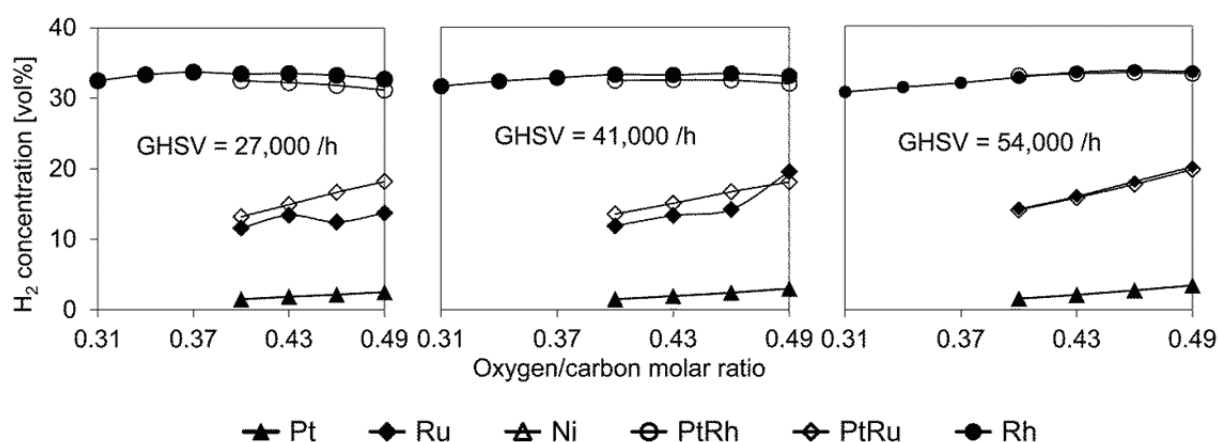

Figure 3　H$_2$ concentration on all six catalysts as a function of the O$_2$/C molar ratio, H$_2$O/C molar ratio = 1.9, at different mean GHSVs, NExBTL diesel fuel

In Figure 3 the influences of the O$_2$/C molar ratio at three different mean GHSVs on the catalytic activity and the stability of the catalysts from this work and the reference catalyst are shown. The pre-aged catalysts from the first three sequences were not replaced. So, the accelerated aging experiment continued. It becomes obvious from Figure 3 on the right that the bimetallic catalyst PtRh/γ-Al$_2$O$_3$ remained as active as the reference catalyst during the fourth sequence. H$_2$ concentrations were in the range between 34 and 33 vol% and almost identical to those of the reference catalyst Rh/γ-Al$_2$O$_3$. The addition of Rh by Pt did not lead to any decrease in the catalytic activity although the trend for the monometallic catalyst Pt/γ-Al$_2$O$_3$ in Figure 3 would suggest this conclusion. As during the first three

sequences the H_2 concentrations of Pt/γ-Al$_2$O$_3$ were very low showing only values between 3 and 2 vol%. In Figure 3 on the right the H_2 concentrations of the bimetallic sample PtRu/γ-Al$_2$O$_3$ and the monometallic catalyst Ru/γ-Al$_2$O$_3$ were very similar. They started at approx. 20 vol% and decreased to 14 vol% at an O_2/C molar ratio of 0.40. Obviously, a significant deactivation of these samples occurred under the rough conditions of the fourth sequence. As can be seen in Figure 3 in the middle and on the left, the deactivation of the catalyst Ru/γ-Al$_2$O$_3$ proceeded. It revealed H_2 concentration gradients between 20 and 12 vol% at a GHSV of 41,000 h^{-1} and between 14 and 12 vol% at a GHSV of 27,000 h^{-1}, respectively. The H_2 concentrations of the sample Pt/γ-Al$_2$O$_3$ remained at their very low level in the range of 3 to 2 vol%. In both figures (middle and left), a slight deactivation of the bimetallic catalyst PtRh/γ-Al$_2$O$_3$ could be observed. H_2 concentrations slightly decreased from the range of 34 to 33 vol% to the level of 32 vol% and 31 to 32 vol%, while the concentrations of the reference catalyst remained constant. Nevertheless, catalyst PtRh/γ-Al$_2$O$_3$ confirmed the conclusion drawn from the results of the first three sequences that it is a promising candidate for the autothermal reforming of BTL diesel fuel with high initial catalytic activity and only marginal signs of deactivation under rough reaction conditions.

In the following, the reducibility of the catalysts from this work will be analyzed with the aid of measurements from temperature-programmed reduction. Figure 4 on the left shows the profiles from the temperature programmed reduction of the fresh catalysts Ni/γ-Al$_2$O$_3$, Pt/γ-Al$_2$O$_3$, Ru/γ-Al$_2$O$_3$, PtRh/γ-Al$_2$O$_3$ and PtRu/γ-Al$_2$O$_3$, before they were subjected to the evaluation pattern. Again for comparison reasons, the corresponding TPR profile of the reference catalyst Rh/γ-Al$_2$O$_3$ is added. The profile **a** of fresh catalyst Ni/γ-Al$_2$O$_3$ shows a very broad signal in the temperature range between 300 and 900 °C, which can attributed to the formation of solid-state solutions of nickel-aluminum-oxide [6]. This signal has a comparatively high intensity, which points at a high reducibility of the fresh sample. The finding stands in sharp contrast to the very low catalytic activity of Ni/γ-Al$_2$O$_3$ for the autothermal reforming of NExBTL diesel. The profile **b** of the catalyst Pt/γ-Al$_2$O$_3$ does not show any reduction signal at all. This means that this sample does not possess any reducibility, which can be detected by temperature programmed reduction, and thus that it is only marginally able to catalyze the autothermal reforming of NExBTL diesel fuel by adsorbing and releasing electrons. This result is well consistent with the comparatively low initial catalytic activity of Pt/γ-Al$_2$O$_3$. In the literature [7], the reduction of platinum oxide is reported at a temperature of approx. 250 °C. In the case of the catalyst Ru/γ–Al$_2$O$_3$, the TPR profile **c** shows a weak shoulder at 105 °C and a more pronounced peak at 145 °C. In the literature [8], the weak shoulder is assigned to the conversion of RuO$_3$ to RuO$_2$, while the main peak is explained by the reduction of RuO$_2$ to elementary Ru. In the profile **e** of the fresh catalyst PtRu/γ-Al$_2$O$_3$ very similar signals for the consumption of H_2 were detected at temperatures of 103 and 139 °C, respectively. As in the case of catalyst Ru/γ-Al$_2$O$_3$, they can be explained by the conversion of RuO$_3$ to RuO$_2$ and the reduction of RuO$_2$ to elementary Ru [9]. No interaction between Ru and Pt particles possibly forming a new joint phase was detected. This is in accordance with results from the literature [10]. The overall intensity of both peaks of PtRu/γ-Al$_2$O$_3$ in profile **e** is slightly lower than that of the monometallic sample Ru/γ-Al$_2$O$_3$ in profile **c**. That means that the addition of Pt to the Ru-based

catalyst lowered the reducibility in the fresh state. This graduation is in good accordance with the initial H_2 concentrations of these both catalysts showing initial values of 31 vol% (Ru/γ-Al$_2$O$_3$) and 27 vol% (PtRu/γ-Al$_2$O$_3$), respectively. The largest consumption of H_2 during the TPR experiments with the fresh catalysts was observed in the case of sample PtRh/γ-Al$_2$O$_3$. In profile **d** two very pronounced signals at temperatures of 83 and 150 °C were identified, which can be attributed to the reduction of a three-dimensional Rh$_i$O$_x$ phase or a dispersed two-dimensional Rh$_i$O$_x$ phase on γ-Al$_2$O$_3$ [11]. The overall intensity of these signals is even significantly higher than that of the signals of the monometallic catalyst Rh/γ-Al$_2$O$_3$ (cf. profile **f**). Also in this case no interaction between the two metals Pt and Rh forming a joint phase could be detected in profile **d**. The observed outstanding reducibility of the fresh sample PtRh/γ-Al$_2$O$_3$ is in good accordance with its very high initial catalytic activity with H_2 concentrations in the range of 36 to 35 vol%. Figure 4 on the right shows the profiles from the temperature programmed reduction of the aged catalysts Ni/γ-Al$_2$O$_3$, Pt/γ-Al$_2$O$_3$, Ru/γ-Al$_2$O$_3$, PtRh/γ-Al$_2$O$_3$ and PtRu/γ-Al$_2$O$_3$, after they were subjected to the evaluation pattern as described above. A comparison of the figures on the left and on the right makes obvious that in any case the profiles of the fresh and aged catalysts are very similar with respect to the position of the respective peaks. Profile **a** of the aged catalyst Ni/γ-Al$_2$O$_3$ again shows the broad signal between 300 and 900 °C. Again, no H_2 was consumed by the catalyst Pt/γ-Al$_2$O$_3$. In the profiles **c** and **e** of the catalysts Ru/γ-Al$_2$O$_3$ and PtRu/γ-Al$_2$O$_3$ the weak shoulder at approx. 130 °C and the more pronounced peaks at 160 and 145 °C, respectively, can be rediscovered. Again as in the case of the fresh samples, the overall intensity of the two peaks of the aged sample PtRh/γ-Al$_2$O$_3$ (98 and 144 °C) is by far highest. The only difference is that for the aged catalyst the peak at 98 °C is less pronounced than it was in the case of the fresh catalyst PtRh/γ-Al$_2$O$_3$. For the catalyst Ru/γ-Al$_2$O$_3$ a significant decrease in the overall intensity of the weak shoulder and the main peak could be detected after the sample was run in the evaluation pattern indicating a loss in reducibility. This is in good agreement with the observed deactivation of this catalyst in the course of the evaluation pattern. However with all other catalyst, the overall intensities of fresh and aged samples were comparable. The rough reaction conditions applied during the evaluation pattern did not significantly lower the reducibility of the active phases of these catalysts. This is in contradiction to the deactivation phenomena, which were observed with the catalysts Pt/γ-Al$_2$O$_3$, PtRu/γ-Al$_2$O$_3$ and PtRh/γ−Al$_2$O$_3$.
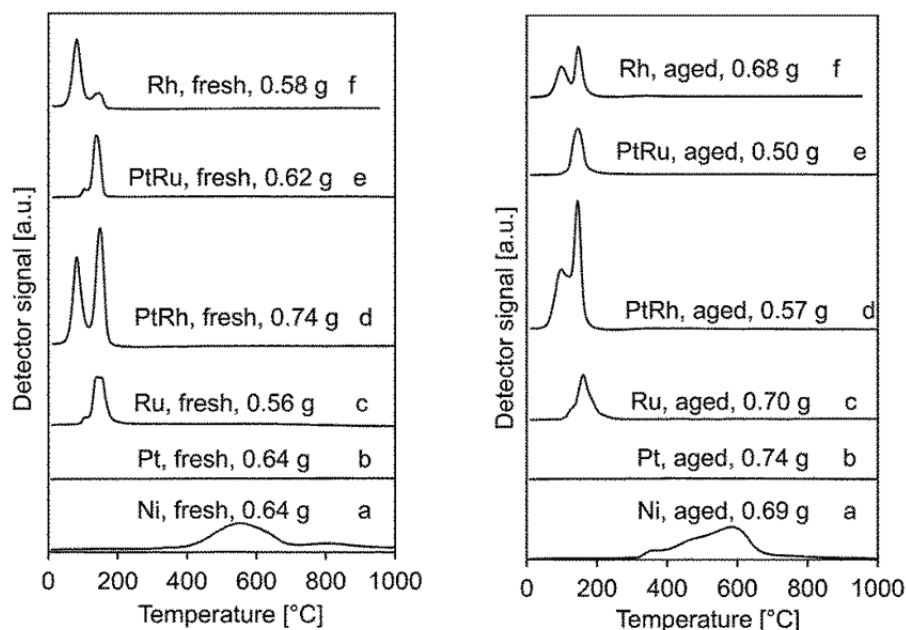
Figure 4   TPR profiles of fresh (left) and aged (right) catalysts Ni/γ-Al$_2$O$_3$, Pt/γ-Al$_2$O$_3$, Ru/γ-Al$_2$O$_3$, PtRh/γ-Al$_2$O$_3$, PtRu/γ-Al$_2$O$_3$ and Rh/γ-Al$_2$O$_3$, H$_2$ consumption is displayed as a function of temperature
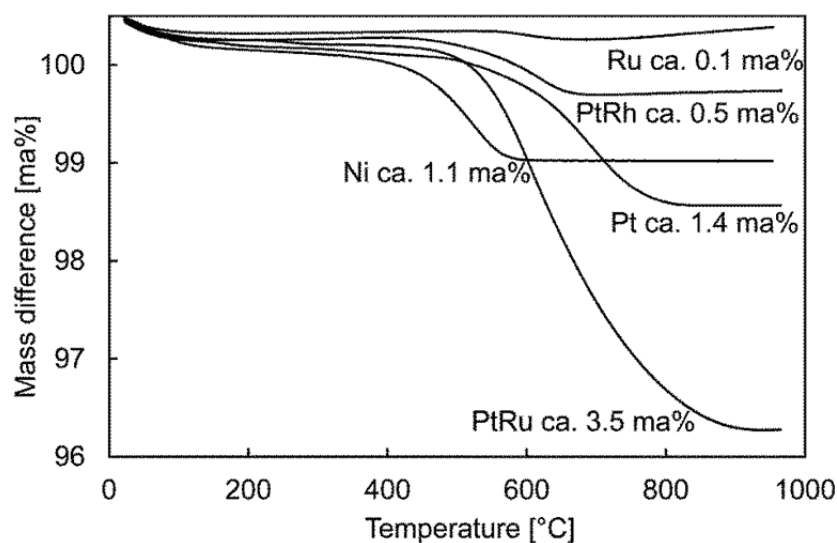
Figure 5   Diagram for the thermogravimetric investigation of aged catalysts: Pt/γ-Al$_2$O$_3$, Ru/γ-Al$_2$O$_3$, Ni/γ-Al$_2$O$_3$, PtRh/γ-Al$_2$O$_3$ and PtRu/γ-Al$_2$O$_3$

In the next subsection, the results of thermogravimetric methods try to shed additional light on causes for the reduced H$_2$ concentrations of the samples in this contribution. The catalysts were heated to temperatures of almost 950 °C in a stream of air while the change in mass was simultaneously determined. The goal was to quantitatively investigate whether carbon-containing deposits were formed on the surfaces of the five catalysts in this study. It becomes obvious in Figure 5 that in the cases of the catalysts Pt/γ-Al$_2$O$_3$, Ni/γ-Al$_2$O$_3$ and PtRu/γ-Al$_2$O$_3$ significant mass losses were detected during the thermogravimetric analyses in the temperature range between 500 and 800 °C. They

amounted to 1.4 ma% for Pt/γ-Al$_2$O$_3$, 1.1 ma% for Ni/γ-Al$_2$O$_3$ and even 3.5 ma% for PtRu/γ-Al$_2$O$_3$. The analysis of the off-gases by means of mass spectrometry revealed high concentrations of carbon dioxide in the temperature range between 500 °C and 800 °C. Cheng et al. [12] found in their work a combustion temperature of coke on Rh/γ-Al$_2$O$_3$ of 600 °C. Therefore, it can be derived that the observed mass losses are due to the burn-off of carbon-containing components from the surface of the catalysts which were formed during experiments on autothermal reforming. Forzatti and Lietti [13] describe how the carbon-containing deposits diminish the catalytic activity, sometimes strongly, since they accumulate on the active catalyst centers so that the latter are no longer accessible for the reactants in autothermal reforming. For the catalysts Pt/γ-Al$_2$O$_3$ and PtRu/γ-Al$_2$O$_3$ from this work, the detected carbonaceous deposits can explain the observed loss in catalytic activity of these samples during the evaluation pattern. The thermogravimetric investigation of the catalysts Ru/γ-Al$_2$O$_3$ and PtRh/γ-Al$_2$O$_3$ showed only minor carbon-containing deposits on the catalysts' surfaces. Therefore, correlations between these findings and the catalytic activities of the catalysts cannot be derived.

Conclusions

Of the samples tested, PtRh/γ-Al$_2$O$_3$ was found to be the most active and robust catalyst for the autothermal reforming of NExBTL diesel fuel. H$_2$ concentrations were in the range of 35 - 36 vol% and decreased only slightly when the evaluation pattern was applied. In contrast, Pt/γ-Al$_2$O$_3$ showed the strongest deactivation. Ni/γ-Al$_2$O$_3$ was not active at all. As described above in detail, decreased reducibilities of the active phases and coke depositions on the catalyst surfaces can be adduced to explain the deactivation phenomena observed with the catalysts from this work.

References

[1]   Adewale P, Dumont M-J, Ngadi M. Recent trends of biodiesel production from animal fat wastes and associated production techniques. Renewable and Sustainable Energy Reviews 2015;45:574-88. DOI: 10.1016/j.rser.2015.02.039

[2]   Dai Y-M, Wu J-S, Chen C-C, Chen K-T. Evaluating the optimum operating parameters on transesterification reaction for biodiesel production over a LiAlO2 catalyst. Chemical Engineering Journal 2015;280:370-6. DOI: 10.1016/j.cej.2015.06.045

[3]   Maneerung T, Kawi S, Wang C-H. Biomass gasification bottom ash as a source of CaO catalyst for biodiesel production via transesterification of palm oil. Energy Conversion and Management 2015;92:234-43. DOI: 10.1016/j.enconman.2014.12.057

[4]   Huber GW, O'Connor P, Corma A. Processing biomass in conventional oil refineries: Production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. Appl. Catal., A 2007;329:120-9. DOI: 10.1016/j.apcata.2007.07.002

[5]   Pasel J, Wohlrab S, Kreft S, Rotov M, Löhken K, Peters R, et al. Routes for deactivation of different autothermal reforming catalysts. J. Power Sources 2016;325:51-63. DOI: 10.1016/j.jpowsour.2016.06.005

[6]   Li C, Chen Y-W. Temperature-programmed-reduction studies of nickel oxide/alumina catalysts: effects of the preparation method. Thermochimica Acta 1995;256:457-65. DOI: 10.1016/0040-6031(94)02177-P

[7]   Ebitani K, Hattori H. Combined Temperature-Programmed Reduction (TPR)- Temperature-Programmed-Desorption (TPD) Study od Supported Platinum Catalysts. The Chemical Society of Japan 1991;64:2422-7.

[8]   Bianchi CL. TPR and XPS investigations of Co/Al$_2$O$_3$ catalysts promoted with Ru, Ir and Pt. Catalysis Letters 2001;76:3-4.

[9]   Nurunnabi M, Murata K, Okabe K, Inaba M, Takahara I. Performance and characterization of Ru/Al2O3 and Ru/SiO2 catalysts modified with Mn for Fischer–Tropsch synthesis. Appl. Catal., A 2008;340:203-11. DOI: 10.1016/j.apcata.2008.02.013

[10]   Bi J-L, Hong Y-Y, Lee C-C, Yeh C-T, Wang C-B. Novel zirconia-supported catalysts for low-temperature oxidative steam reforming of ethanol. Catal. Today 2007;129:322-9. DOI: 10.1016/j.cattod.2006.11.027

[11]   Yao HC, Japar S, Shelef M. Surface interactions in the system RhAl$_2$O$_3$. J. Catal. 1977;50:407-18. DOI: 10.1016/0021-9517(77)90053-7

[12]   Cheng CK, Foo SY, Adesina AA. Carbon deposition on bimetallic Co–Ni/Al2O3 catalyst during steam reforming of glycerol. Catal. Today 2011;164:268-74. DOI: 10.1016/j.cattod.2010.10.040

[13]   Forzatti P, Lietti L. Catalyst deactivation. Catal. Today 1999;52:165-81. DOI: 10.1016/S0920-5861(99)00074-7