Steam- and autothermal-reforming of n-butanol over Rh/ZrO2 catalyst

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Abstract

Steam reforming (SR) and autothermal reforming (ATR) of n-butanol was studied over 0.5 wt% Rh/ZrO2 catalyst at 500, 600 and 700 °C, atmospheric pressure, steam to carbon (S/C) molar ratio of 4 and oxygen to carbon (O2/C) molar ratio of 0.1. The influence of the O2/C ratio on performance was also carried out at 500 °C. Catalyst performance, i.e. conversion, product distribution and short-term stability, was compared with plain ZrO2 support to derive a reaction network, including contributions of reactions in the gas phase, on the support and on Rh. At 500 and 600 °C the catalyst deactivated very rapidly for WGS and hydro-isomerization reactions, slightly less rapidly for reforming and significantly slower for dehydration and dehydrogenation reactions. Increasing temperature and oxygen concentration improved catalyst stability. Rh/ZrO2 showed promising performance at 700 °C with complete conversion and hydrogen yield, 70% of theoretical maximum, decreasing over 21 h with not more than 8 and 1% for SR and ATR, respectively. Deactivation of the catalyst for reforming is caused by carbon deposition on and near the Rh particles. At 700 °C, coke forms via gas phase reactions, while catalytic reactions on the surface mainly contribute at 500 and 600 °C.

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1. Introduction

Hydrogen is an essential part of present and future energy systems. It is e.g. seen as an energy carrier for vehicles powered with fuel cells, but also as an essential reactant needed for hydro-deoxygenation (HDO) of biomass based feedstock. The conventional method of hydrogen production is steam reforming of natural gas. This is obviously not sustainable and renewable alternatives are required. Bio-hydrogen, i.e. hydrogen from biomass, can be produced via several process routes, including direct gasification of biomass as well as catalytic conversion of biomass-based intermediates, e.g. flash pyrolysis oil [1,2] containing amongst others phenol [3–7], ethanol [8–11] or butanol based on fermentation, via the ABE fermentation process [12–16]. Pyrolysis oil also contains enough butanol [17] to make it an interesting model compound for study.

The reforming of light alcohols, methanol and ethanol, has been extensively studied and reviews are available [8,18]. There are only a few publications about steam reforming of butanol, whereas autothermal reforming of butanol as a pure compound has not been reported at all to our knowledge. Hu and Lu studied steam reforming of butanol using co-precipitated Ni/Al catalysts [19], as did Bimhela et al. with various Ni loadings [20] and also with Ni catalysts modified with Mg or Cu [21], while Medranos et al. [22] applied Ni/Al catalysts in fluidized bed configuration. Le Valant et al. studied steam reforming of pure butanol [10] as well as butanol impurity in ethanol steam reforming [11], using a Rh catalyst supported on a MgAl2O4/Al2O3 support. Cai et al. have focused more on autothermal reforming of acetone–butanol–ethanol mixtures reported [14–16], but have also reported on steam reforming of butanol over various Co based catalysts [13].

The aim of this work is to assess hydrogen production via steam reforming of n-butanol over Rh/ZrO2 catalyst. Zirconia and zirconia mixed oxide supported catalysts have shown promising performance for reforming of ethanol with Rh [9] and other oxygenates with Rh [3–7,23,24] and with other metals [25,26]. A reaction network for the reforming of n-butanol, including the different contributions of reactions on Rh, the support and in the gas phase is proposed. Furthermore, the effect of adding oxygen to the feed on the hydrogen production and catalyst stability in the first hours of operation is also investigated, in order to understand the reason for the change in performance as compared to the virgin catalyst. This information can guide future research in developing stable,
active and selective catalysts for the reforming of heavy alcohols and other bio-based reactants.

2. Materials and methods

2.1. Chemical equilibrium calculations

Chemical equilibrium calculations were carried out using the HSC Chemistry 5.11 software by Outotec [27]. The calculation method was based on the minimization of Gibbs free energy. Steam to carbon (S/C) ratio was varied between 0 and 4 with increments of 0.25 and oxygen to carbon (O₂/C) ratios was varied between 0 and 1 with increments of 0.1. Temperature was varied from 100 to 900 °C with increments of 10 °C and pressure was kept constant at 1 atm. The components considered in the calculations were the feed components n-butanol, water and oxygen, C₄ products butyraldehyde, 1-butene and n-butyne, C₂ products propene and propane, C₂ products ethyne, ethene and ethane, C₁ products methane, carbon monoxide and carbon dioxide, as well as solid carbon in both graphitic and amorphous form, which is relatively unfavorable.

2.2. Catalyst preparation and characterization

The Rh catalyst was prepared by vacuum assisted dry impregnation from 10 wt.% Rh(NO₃)₃ solution diluted in 5 wt.% nitric acid (Sigma–Aldrich) to obtain 0.5% Rh by weight. The ZrO₂ support (MEL Chemicals EC0100) was ground and screened to particle size 0.25–0.42 mm and calcined in synthetic air (20% O₂/Ar, Aga, 99.99%) at 850 °C for 16 h. Prior to impregnation, the support was dried overnight at 90 °C and 1 h under vacuum at 100 °C. The catalyst was kept under vacuum during the impregnation and subsequent drying, first at room temperature overnight, then at 40 °C for 1.5 h and 60 °C for 0.5 h, before being calcined at 850 °C for 1 h (heating rate 80 °C/h).

The Rh loading of the fresh catalyst was determined by X-ray fluorescence spectrometer (Philips PW 1480 XRF) equipped with UniQuant 4–software. The BET surface area of the support and H₂ chemisorption were performed with Coulter Omnisorp 100 CX, using methods described elsewhere [28,29].

2.3. Reaction experiments

Tubular quartz reactor with inner diameter 7 mm was packed with 0.1 g of the catalyst sandwiched between two 0.3 g layers of SiC grains and placed in a three-zone furnace equipped with a temperature controller (Carbolite). The catalyst bed temperature was measured with a thermocouple inserted in a quartz pocket (outer diameter 3.1 mm) running through the catalyst bed. To limit the empty space in the reactor, the inner diameter of the reactor tube was reduced to 4 mm after the catalyst bed and the outer diameter of the thermocouple pocket was widened to 6 mm above the catalyst bed. With the thermocouple in place, the height of the catalyst layer was 2 mm.

The reactor was heated to 600 °C under Ar (Aga, 99.999%) flow, followed by reduction in 50% H₂ (Aga, 99.999%) in Ar for 1 h, after which the reactor was flushed with Ar and heated or cooled to the desired reaction temperature in Ar atmosphere.

Distilled water (0.16 ml/min) and n-butanol (0.05 ml/min, Sigma–Aldrich, 99.4%) were fed into separate evaporators (180 °C) by high performance liquid chromatography pumps (HPLC-pumps, Agilent Technologies), equipped with micro vacuum degassers (Agilent Technologies). Before introduction to the reactor, the vaporized feed was diluted with Ar, and mixed with synthetic air in the case of ATR experiments. The total flow rate of the reaction mixture in the inlet temperature of the reactor (180 °C) was 650 ml/min and 700 ml/min during SR and ATR experiments, respectively, translating to GHSV 101,000 and 109,000 h⁻¹ for SR and ATR, respectively, and implying a contact time of typically 20 ms. The composition of the reaction mixture by volume was 3.1% butanol, 50% H₂O and 47% Ar for SR, and 2.9% butanol, 47% H₂O, 1.3% oxygen, 5.4% N₂ and 44% Ar for ATR. The temperature of the catalyst bed was kept constant by adjusting the set-point temperature of the furnace, during typically 3 h.

External diffusion limitation can be excluded based on calculation of Mears’ criterion CM, resulting in CM ≈ 7.8 × 10⁻⁵ ≪ 0.15. Occurrence of any internal diffusion limitation for steam reforming at 500 °C was estimated with the Weisz–Parter criterion, CWP based on the apparent kinetics, resulting in CWP = 40, indicating that the influence of internal concentration on the reaction rates is significant. Naturally, any influence of internal diffusion will become more dominant when increasing the temperature to 600 and 700 °C. Since the catalyst and support used in all the experiments is the same, results can be compared with one another, but kinetics cannot be determined based on the data reported, obviously.

For comparative purposes, and in order to see which products originate from surface reactions on the support or from gas phase reactions, experiments were also carried out with pure ZrO₂ and blank experiments were done using a bed of 0.6 g SiC filler. Stability of the catalyst was tested for 23 h at 700 °C under both SR and ATR conditions and also 600 °C under ATR conditions.

After the experiment, the reactor was flushed with Ar and cooled down to room temperature. The amount of carbon on the used catalysts was determined by temperature programmed oxidation (TPO) in the same setup without opening the reactor in between. The catalyst was heated at 5 °C/min to 800 °C in 3% O₂ in Ar and N₂ (650 ml/min), kept at 800 °C for 1 h and then allowed to cool down. The only observed product during TPO was CO₂.

2.4. Product analysis and calculation

The product gas mixture leaving the reactor was diluted with N₂ (1600 ml/min, NTP) and analyzed using an online Fourier transform infrared (FTIR) spectrometer (Gasmet™) equipped with a Peltier-cooled mercury-cadmium-telluride (MCT) detector and multicomponent analysis software (Calcmet). The sample cell was kept at 180 °C. The compounds analyzed were H₂O, CO, CO₂, CH₄, acetylene, ethylene, ethane, and propylene, all isomers of butene, butanol, butyraldehyde and butyric acid. It was not possible to analyze butane and propane together with the C₄ oxygenates because of excessive interference in the analysis. Downstream of the FTIR analysis, water and any other condensable compounds were removed in a Peltier-cooled PSS-10 gas drier (M&Co) and the dry gas was further analyzed with a set of GMS810 gas analyzers (SICK), with modules for H₂, CO₂, CO and CH₄. Further downstream, the flow rate of the dry gas was measured using a volumetric gas meter. After the experiment, a sample was taken from the condensate collected by the gas drier and analyzed with GC/MS for a qualitative analysis of the condensable compounds produced.

The hydrogen yield was calculated based on the theoretical stoichiometric maximum of butanol conversion to H₂ and CO₂ (H₂:butanol = 12 mol/mol).

\[ Y_{H_2} = \frac{F_{H_2, out}}{F_{butanol, in}} \times 12 \]

The yields of components other than H₂ were defined on C₁ basis. Yield of compound i is therefore the ratio of the moles of carbon in compound i [molar flow of compound i] in the product in moles/min,
$F_{\text{out}}$, multiplied by the carbon number of the compound, $N_C$, to the total molar amount of carbon in the feed (mol $C_i$/mol $C_{\text{in}}$):

$$Y_i = \frac{F_{\text{out}} N_C}{F_{\text{in}} C_{\text{in}} \times 4}$$

(2)

Products that were not analyzed by the online FTIR or the GMS810 analyzers, were lumped as unidentified products. The yield of unidentified products was calculated from the mass balance.

3. Results

3.1. Chemical equilibrium based on thermodynamics

In Fig. 1A, a plateau of maximal H$_2$ yield is observed being widest with S/C ratio 4 (mol/mol) between 450 and 730 °C, motivating the investigated temperature range in this study. Fig. 1B indicates decreasing hydrogen yield with increasing O$_2$/C ratio, when S/C ratio is 4. It can be calculated that, assuming chemical equilibrium, the reactions become thermo-neutral ($\Delta H = 0$) at O$_2$/C ratio 0.8 (mol/mol). Products present at equilibrium were exclusively H$_2$ and CO$_2$, as well as minor amounts (<0.1%) of CO, CH$_4$ and solid carbon, graphitic carbon constituting over 94% of total solid carbon in all temperatures. At S/C = 4, the CO$_2$ yield is close to 100% within the investigated temperature range 500–700 °C, as is the H$_2$ yield for SR. ATR at O$_2$/C = 0.1 results in typically 93% H$_2$ yield in the same temperature range.

3.2. Catalyst characterization

The BET surface area of the ZrO$_2$ support was 42 m$^2$/g and the total pore volume was 0.15 cm$^3$/g. The metal loading measured by XRF was 0.57 wt.%, similar to the targeted loading of 0.5%. Rh dispersion was 22% according to H$_2$ chemisorption.

3.3. Reaction experiments

3.3.1. Conversion and yield of reforming reaction products

Fig. 2 shows butanol conversion and hydrogen yield for SR and ATR at 500, 600 and 700 °C, for Rh/ZrO$_2$ as well as bare ZrO$_2$ and in the absence of any catalyst. When increasing the temperature from 600 to 700 °C in SR, conversion via homogeneous pyrolysis reactions in the gas phase increases significantly. During ATR, the rate of homogeneous oxidation reactions is significantly higher as compared to SR already at 500 °C. At 500 and 600 °C, Rh/ZrO$_2$ shows initially higher conversion than the ZrO$_2$, declining to similar levels after an onset period. Fig. 2E and F show that at 700 °C during both SR and ATR, the initial conversion is complete on both Rh/ZrO$_2$ and ZrO$_2$. The conversion over Rh/ZrO$_2$ remains complete during 23 h, whereas the conversion on ZrO$_2$ collapses to the level of blank experiments in 15 min.

Fig. 3 shows the yields of CO and CO$_2$ for SR and ATR at 500, 600 and 700 °C, for Rh/ZrO$_2$ as well as bare ZrO$_2$ and in the absence of any catalyst. The hydrogen yield curves in Fig. 2 and the yields of CO$_2$ in Fig. 3 demonstrate that reforming, partial oxidation and WGS reaction, all contributing to the formation of H$_2$, CO and CO$_2$, require the presence of Rh, as expected. Regarding the yields of these gases, ZrO$_2$ performs similar to gas phase reactions, the minor yields of carbon oxides probably resulting from thermal decomposition and/or combustion reactions. Over the Rh/ZrO$_2$ catalyst at 700 °C and initially at 600 °C, the main products are hydrogen and carbon oxides. However, the yield of CO is higher than expected based on thermodynamic equilibrium (Fig. 1) and conversely the CO$_2$ and H$_2$ yields are lower than at the equilibrium. This indicates that CO$_2$ and H$_2$ are formed via relatively slow consecutive reaction, converting CO. At 700 °C and also initially at 600 °C, the H$_2$ and CO$_2$ yields decrease, while CO yield increases, indicating decline of WGS activity.

3.3.2. Yield of butenes, butyraldehyde and unidentified products

The yields of 1-butene and other butene isomers in Fig. 4 and the yields of butyraldehyde and unidentified products in Fig. 5, show that during SR on ZrO$_2$ at 500 and 600 °C, 1-butene is the main product. At 700 °C, initially also other butene isomers are observed during both SR and ATR on ZrO$_2$ and the combined butene yields account for the conversion, but the yields collapse very rapidly to the level of blank experiments. In contrast, even after deactivation, the 1-butene and butyraldehyde yields at 500 and 600 °C consider­ably differ from blank experiment, indicating that some catalytic activity of ZrO$_2$ remains, despite the fact the conversion declines to blank level, as is observed during ATR in Fig. 2B and C. During ATR at 500 °C on ZrO$_2$, the main product is butyraldehyde, indicating oxidative dehydrogenation takes place on ZrO$_2$. During ATR at 600 °C on ZrO$_2$, initially 1-butene is the main product, but its yield decreases with time-on-stream while the yields of both butyraldehyde and unidentified products increase.

Fig. 4A and B shows high initial yields of butenes on the Rh cata­lyst at 500 °C indicating that Rh enhances dehydrogenation. The butene yield at 500 °C is quite steady during ATR, but declines during SR. On Rh/ZrO$_2$ at 500 °C, butyraldehyde yield (Fig. 5A and B) is higher during SR, as compared to ZrO$_2$, but lower during ATR. At 600 °C, the

![Fig. 1. Thermodynamic hydrogen yield. Hydrogen yield as a function of temperature and (A) S/C ratio during SR and (B) O$_2$/C ratio with S/C = 4.](image-url)
yields of both butenes (Fig. 4C and D) and butyraldehyde (Fig. 5C and D) follow similar trends during both SR and ATR: the yields are initially close to zero, then increase as the deactivation of reforming activity proceeds and finally decrease again as the dehydration and dehydrogenation activities also decline. On Rh/ZrO₂ at 700 °C, neither intermediate is detected.

Isomerization of butenes is observed on Rh/ZrO₂ during both SR and ATR at 500 °C (Fig. 4A and B). This can probably be attributed to hydroisomerization activity of Rh [30]. On ZrO₂, isomerization is observed only at higher temperature (600 and 700 °C) during both SR and ATR (Fig. 4C–F). In all cases, both on Rh/ZrO₂ and ZrO₂, the isomerization products disappear quickly with time-on-stream, indicating that isomerization is particularly sensitive to catalyst deactivation.

On Rh/ZrO₂ the yield of unidentified products, estimated based on the mass balance, decreases as a function of temperature during SR and is always close to zero at 700 °C (Fig. 5A–C) whereas during ATR the yields of unidentified products are low at all three temperatures. On ZrO₂, the yield of unidentified products exhibits an increasing trend as a function of temperature both in SR and ATR. At 700 °C, the unidentified yield is initially very low, but rapidly rises to the high level observed in blank experiments, indicating that at 700 °C the unidentified products are in fact formed in the gas phase and initially converted by ZrO₂, which however deactivates rapidly. Unlike ZrO₂, Rh/ZrO₂ is able convert the gas phase products at 700 °C without major apparent deactivation.

3.3.3. The effect of O₂/C ratio at 500 °C with Rh/ZrO₂

According to Fig. 6A, increasing O₂/C ratio slows down the decline of conversion and the final conversion is also higher. With O₂/C ratio 0.8, conversion remains complete during 3 h. However, ATR conversion is stabilizing after initial deactivation and the remaining conversion is governed by gas phase reactions, as already discussed for the result with O₂/C ratio 0.1 in Fig. 3B.

Comparing the H₂ yields in Fig. 6B with the equilibrium yield in Fig. 1, it can be concluded that equilibrium was not achieved, as otherwise the H₂ yield would have collapsed with increasing O₂/C ratio. Fig. 6C shows that increasing the O₂/C ratio slows down the decline of CO yields, indicating slower deactivation of reforming activity. Fig. 6D shows that increasing the O₂/C ratio increases the CO₂ yield, due to enhanced oxidation of CO, as expected.

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Fig. 2. Evolution of conversion and H₂ yield during reforming experiments. The figures on the left are from steam reforming and the figures on the right are from autothermal reforming experiments. The temperature of the data is indicated in the upper right corner of each graph. Please note the different time scales.
3.4. TPO of spent catalysts

TPO provides information on both amount and reactivity of the deposited carbon. A typical TPO curve is shown in Fig. 7 for Rh/ZrO₂ and ZrO₂ after SR at 500 °C. A sharp peak is observed with Rh/ZrO₂ around 300 °C, attributed to carbon deposits on noble metal particles in literature [26,31,32]. There is also a shoulder observed at 380 °C, matching the main peak of ZrO₂ TPO, attributed to deposits or surface species on the ZrO₂ support with relatively high reactivity, induced by the presence of hydrogen and/or oxygen in the deposit [31,33]. The peaks above 500 °C are attributed to less reactive and more graphitic carbon species on Pt/Al₂O₃ used for reforming of hydrocarbons [31] and it seems reasonable to assume that the assignment holds for our case. In further discussion, the peak corresponding to carbon on/near the Rh particles will be referred to as Cₘₚ peak and the peak or shoulder corresponding to reactive deposits on ZrO₂ will be referred to as C₂₂. This is allowed, as the experimental conditions of the TPO experiments were identical. The carbon loadings on the catalysts are presented in Fig. 8, divided into the three different carbon species. The amount of graphitic coke is based on integration of the high temperature (>500 °C) peaks. The sum of the amounts Cₘₚ and C₂₂ is calculated by integrating their combined peak (<500 °C). The Cₘₚ and C₂₂ amounts are estimated based on deconvolution of the combined peak using OriginPro 9 software. Example of the deconvolution for the TPO Rh/ZrO₂ after reaction at 500 °C is shown in Fig. 7.

Fig. 8A shows that coke deposition on ZrO₂ increases with temperature from 500 to 600 °C, without significant further increase at 700 °C. On ZrO₂ more coke is deposited during ATR than during SR, surprisingly. Fig. 8B shows that on Rh/ZrO₂, coke deposition decreases with increasing temperature, and by oxygen addition, especially at 600 and 700 °C. The effect of increasing the time-on-stream from 2 to 3 h to over 20 h is significant on Rh/ZrO₂, whereas a very small effect is observed for ZrO₂. The Cₘₚ amounts are very small after SR and ATR at 700 °C. At 600 °C, adding oxygen reduces the amount of Cₘₚ on short term. Fig. 8C shows that total carbon deposition on Rh/ZrO₂ at 500 °C is not influenced when O₂/C ratio is changed from 0 to 0.1, which is the ratio used in most of the ATR experiments. However, further addition of oxygen decreases coke deposition and a very low amount (0.5 mmol/gcatalyst) is observed with O₂/C ratio 0.8. At 500 °C, a maximum in Cₘₚ amount is obtained with O₂/C ratio 0.1. Moreover, the amount of Cₘₚ with O₂/C ratio
0.8 is insignificantly small. Coke deposition was in all cases much higher as predicted by thermodynamic equilibrium calculation.

3.5. Qualitative analysis of gas dryer condensate

The organic fraction in the condensate was analyzed using GC–MS and the product peaks were assigned using the spectral library in the GC–MS software provided by Agilent. For most product peaks, the probabilities of the identification by the library were quite low, so in these cases the species were taken as classes of certain types of products, rather than specific components. Apart from butanol, butyraldehyde and butyric acid, which are also detected in the FTIR analysis, samples from all experiments contained several small peaks of branched C8 and C12 hydrocarbons, indicating oligomerization reactions. In the condensates of the ZrO2 experiments, also oxygenated C8 and C10 species as well as aromatic hydrocarbons were observed. In the condensate of SR experiments, butyl butanoate was also observed. These observations are indicative for both unidentified products as well as possible reaction pathways.

4. Discussion

4.1. Comparison of catalyst performance to literature

Le Valant et al. [11,10] used 1 wt.% Rh supported on MgAl2O4/Al2O3, reporting no conversion at 675 °C with S/C ratio 2.5. This is not in agreement with our results at 700 °C; even in an empty reactor, the conversion is already ca. 50% with S/C ratio 4 and higher space velocity. This is probably due to differences in experimental conditions, including the higher pressure (2 bar), undiluted feed and use of steel reactors instead of glass. At these conditions the carbon deposition was so rapid that the reactor got blocked in 1 h and this probably accounts for the difference with our results. The S/C ratio had to be lowered to 1 before reaction was observed to mainly butene and various cracking products.

Bimbela et al. [20,21] reported lower conversions and higher selectivity to H2 and CO2, as well as better stability for coprecipitated Ni/Al catalyst as compared to the results in this study. This is probably due to the much higher S/C ratio (14.7) and orders of magnitude smaller space velocities used. Medrano et al. [22] from the
same group studied these catalysts in fluidized bed steam reforming of butanol, resulting in improved stability and feed conversion at the expense of slightly reduced activity toward reforming and WGS as compared to the packed bed used by Bimbela. Hu and Lu [19] also used a NiAl2O3 to study the effect of carbon number and functional groups of feed molecules on steam reforming. Reforming n-butanol with S/C ratio 6 at 400 °C, high conversion and high H2 selectivity were obtained, but also significant selectivity (28%) toward methane was observed, probably due to the use of a space velocity one order of magnitude lower as compared to our study. Butanol reforming with a stoichiometric S/C ratio 1.75 at 600 °C was also tested. At these conditions, less deactivation compared to this work was reported, despite the fact that the rate of coke formation was more than four times higher than reported on Rh/ZrO2 in this work; any deactivation was probably masked by the high conversion in the work of Hu and Lu. Cai et al. [13] compared 7 wt-% Co supported on ZnO, CeO2 and TiO2 for the steam reforming of butanol, reporting high conversion and H2 selectivity at 500 °C and much better stability at 600 °C compared to the results in this work. The order of magnitude smaller space velocity employed by Cai et al. as compared to our work may account for the higher conversion and H2 selectivity. However, coke loadings ranging from two to six times higher than observed in this work were reported.

Comparing the results of this study to previous studies on butanol steam reforming, it should be noted that the catalyst in this study has a very low metal loading, and compared to the feed rate, the catalyst loading in the reactor was also low. As a result, the GHSV in this study system was at least one order of magnitude higher than what was used by others. Still, H2 yields of about 70% of the thermodynamic equilibrium (Fig. 1) were obtained at higher temperatures. This indicated that the Rh/ZrO2 catalyst used in this study exhibits excellent productivity per gram of catalyst and especially per gram metal, compensating for the higher price of Rh as compared to Ni with improved activity [34–36]. Actually, experiments at 700 °C resulted in complete conversion despite the high SV and catalyst deactivation could not be judged anymore. It should be noted that the Rh loading can be even further reduced as internal diffusion limitation is significant. Moreover, the amount of coke deposition reported in this work is very low compared to other studies, making the catalyst system promising for further study.

**Fig. 5.** Evolution of butyraldehyde and unidentified product yields during reforming experiments. The figures on the left are from steam reforming and the figures on the right are from autothermal reforming experiments. The temperature of the data is indicated in the upper right corner of each graph. Please note the different time scales.
Fig. 7. TPO curves of Rh/ZrO2 and ZrO2 after SR at 500°C. The curve for Rh/ZrO2 also shows the deconvolution result with dotted lines.

4.2. Reaction network

Based on our observations and literature on pyrolysis, combustion and partial oxidation reaction mechanisms [37–40], a schematic reaction network presented in Fig. 9 is proposed, which will be used to further discuss the results. The catalyst sites involved in the reactions are suggested for the main reactions. For simplicity, long side reaction paths, such as the coupling reactions of butyraldehyde, have been lumped.

On oxides, dehydration (reaction 2) activity is usually assigned to acid sites and dehydrogenation (reaction 6) to basic sites [23,41]. Dehydrogenation is also expected to proceed on Rh. On ZrO2 supported catalysts, reforming reactions (1, 3 and 7) and WGS have been proposed to take place on the metal-support interface [24,26,42], although for Rh catalysts reaction on the metal only cannot be ruled out. Regarding the side reactions, Rh is known to be active for hydroisomerization of butenes [30]. Isomerization is also known to be catalyzed by strong acid sites [43], and although ZrO2 is only weakly acidic, the observed isomerization over ZrO2 (Fig. 4C and D) can be assumed to take place on acid sites. Oligomerization reactions are catalyzed by both acidic and basic sites for butyraldehyde (reaction 8) [44–47], whereas butene oligomerizes over acidic sites (reaction 5).

On the Rh/ZrO2 catalyst at 500°C, the high initial yields of butenes (Fig. 4A and B) and butyraldehyde (Fig. 5A and B) compared to CO2 (Fig. 3A and B) and H2 (Fig. 2A and B) indicate that the first reaction steps, dehydration and dehydrogenation (reactions 2 and 6, respectively) are initially faster than the reforming reactions (reactions 3 and 7, respectively). Furthermore, very low initial yields of butene and butyraldehyde are obtained at 600 and 700°C, which indicate that the activation energies of reforming reactions are higher than reactions yielding butene and butyraldehyde. Comparing the H2 yields at all temperatures with the thermodynamic equilibrium in Fig. 1, it can be concluded that short contact time prevents equilibration of the WGS reaction (reaction 11), hence meaning that WGS is relatively slow as compared to reforming reactions. Butene yields are higher than butyraldehyde yields for Rh/ZrO2 at both 500 and 600°C for both SR and ATR as shown in Figs. 4 and 5. Therefore, the dehydration route in Fig. 9 is contributing more than the dehydrogenation route. At 700°C for SR and ATR over Rh/ZrO2, neither intermediate is detected, suggesting that either direct reforming (reaction 1) is dominant, or that reforming of butene and butyraldehyde is much faster than dehydrogenation and dehydration. The fact that ZrO2 gives high initial yields of butenes at 700°C, suggests the dehydration pathway contributes more than dehydrogenation, in case the indirect routes are important at 700°C.

4.3. Deactivation and coke formation

The change in product yields with time-on-stream is most obvious at 600°C (Figs. 2–5C and D), indicating that the reaction rates of the different steps in Fig. 9 are differently affected by deactivation. Butene isomer yield in Fig. 4 disappears rapidly and completely,
pronounced (Figs. 2A and B, 3A and B, 4A and B, 6). In short, the catalyst loses activity for isomerization and WGS first, followed by activity for reforming and finally by activity for dehydration and dehydrogenation.

The order in which the different reactions decline provides information about the location of the carbon deposits. On both Rh/ZrO₂ and ZrO₂, the fastest disappearing reaction is isomerization, indicating carbon deposition directly on Rh particles as well as on acidic sites. WGS and reforming reaction also decline rapidly, indicating deposit formation on and close to the Rh particles. Finally the observation that over ZrO₂ dehydrogenation activity of the catalysts declines, while dehydrogenation to lesser extent, indicates that on the ZrO₂ support the deposits are formed on acidic sites and less well on the basic sites. By comparing the CₓHᵧ peak sizes and the degree of deactivation, defined as the difference between the initial and final hydrogen yields, a correlation is apparent at 500 °C for both SR and ATR, shown in Fig. 10A. In contrast, no clear correlation is observed between the deactivation of reforming activity and the total carbon loading. This suggests that the deactivation of Rh/ZrO₂ is indeed determined by the amount of carbon deposits on/close to the Rh particles instead of the total amount of deposits. On ZrO₂, a correlation between the butyraldehyde yield at the end of the experiment and total carbon deposition is shown in Fig. 10B at 700 °C for both SR and ATR. This observation suggests that butyraldehyde is acting as precursors for the CₓHᵧ deposits.

At 500 and 600 °C, Rh/ZrO₂ deactivates almost completely and the total amount of carbon deposited is higher than on ZrO₂. This indicates that presence of Rh enhances carbon deposition, as compared to bare ZrO₂, by enabling a coke formation pathway which does not exist on bare ZrO₂. According to a reaction mechanism reported in literature for other oxygenates on noble metals [26,48], direct reforming proceeds through decomposition of the oxygenate to form alkyl surface species, which can either be reformed or act as precursors for the formation of coke on cannot be reformed sufficiently fast at 500 and 600 °C, explaining the high amounts of CₓHᵧ observed.

In contrast, at 700 °C the reforming and gasification activity is sufficiently high to keep the Rh surface essentially clean, explaining the very low amounts of CₓHᵧ observed at 700 °C in Fig. 8B. However, as seen in Fig. 8A and B, the amount of CₓHᵧ deposited on Rh/ZrO₂ in SR at 700 °C increases considerably between 2.7 and 25 h on stream,
whereas on ZrO₂ the increase is very limited and the resulting total carbon loading lower than on Rh/ZrO₂. A possible explanation for this is that Rh catalyzes the formation of intermediates causing deposits on the support, such as butyraldehyde.

Whereas the amount of unidentified products observed in the gas phase in Fig. 5 is low at 500 and 600 °C, it is very high at 700 °C. As already previously noted, this means that at 700 °C unidentified products are formed in the gas phase before the gases come in contact with the catalyst. Rh/ZrO₂ is capable of converting these components to the desired H₂ and COₓ, but on ZrO₂ they cause the rapid and complete deactivation, which can be observed in Figs. 2–5 and also in the very minor increase in the amount of coke deposited between 2 and 25 h on stream. The coke formation mechanisms at the different temperatures are illustrated in Fig. 11.

The observed carbon deposition is the result of the ratio between deposition and gasification reactions (reactions 9 and 10, respectively). Rh is known to be active for the gasification and combustion of carbon deposits (reaction 10). Comparing the amounts of C_Rh in Fig. 8 shows that C_Rh peak is reduced by increasing temperature and by adding oxygen. This suggests that on the Rh/ZrO₂ catalyst, the removal of the carbon deposits (reaction 10) is enhanced more significantly than the carbon deposition reactions when increasing temperature and O₂ concentration, as can be expected. This improves the stability of the catalyst, evidenced as the near absence of carbon deposits close to the Rh particles, represented by the C_Rh peak for SR at 700 °C. However, this effect is only experienced close to the Rh particles, as the overall amount of deposited carbon and especially C_Zr is still higher than on ZrO₂. For ATR over Rh/ZrO₂ at

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**Fig. 10.** Correlations in deactivation. (A) Change in H₂ yield as a function of CRh peak at 500 °C. (B) Final butyraldehyde yield as a function of total carbon deposition on ZrO₂ at 700 °C.

**Fig. 11.** The proposed coke deposition mechanisms. (A) 500 and 600 °C and (B) 700 °C. Thickness of arrows corresponds to the relative rates of the different reactions.
700 °C the removal is so efficient that even the overall amount of coke is reduced, possibly by oxygen spillover with increased diffusion length. In contrast, Polychronopoulou et al. [6] reported that steam was more efficient than oxygen in removing carbon deposits formed during steam reforming of phenol. This difference is probably due to differences in the support material (pure ZrO₂ compared to Mg–Ce–Zr–oxide) as well as the reactant (butanol compared to phenol).

The requirements for catalyst stability depend on temperature. At 700 °C, good gasification and reforming activity is required to convert the products of gas phase reactions, which is effectively achieved by the Rh/ZrO₂ catalyst studied in this work. At 500 and 600 °C, where the stability of the Rh/ZrO₂ catalyst is not satisfactory, the stability of the catalyst might be improved by either enhancing the gasification functionality of the catalyst to reform the intermediate alkyl species on the metal, for example by tailoring the support material for enhanced water activation [3–7], or by inhibiting the side reactions leading to coke formation, namely oligomerization and decomposition reactions of butyraldehyde on the surface.

5. Conclusions

Rh/ZrO₂ shows promise as a catalyst for reforming of butanol, exhibiting very high H₂ productivity per weight of the catalyst and especially per weight of active metal, despite occurrence of internal diffusion limitation. Also, significantly less coke is deposited as compared to alternative catalysts described in literature so far. The main reaction pathways for butanol reforming are direct reforming and dehydrogenation followed by reforming of butanes and water-gas-shift. Deactivation of WGS activity proceeds very rapidly, followed by deactivation for responsible, whereas the active sites responsible for dehydrogenation of butanol deactivate slower. The deactivation of the Rh/ZrO₂ catalyst for reforming is caused by accumulation of carbon deposits on and near the Rh nanoparticles. Butyraldehyde and condensation products thereof, act as precursors to coke deposition. At 700 °C, the coke precursors originate predominantly from reactions in the gas phase and catalysts stability is governed by the ability of the catalysts to reform these compounds efficiently. At lower temperatures formation of deposits takes place predominantly via reaction on the catalyst surface.

Acknowledgments

Financial support from the Finnish Funding Agency for Technology and Innovation (Tekes) and from Neste Oil is acknowledged. We thank Dr. Kristiina Uusi-Esko for the XRF measurements and Arto Mäkinen for the physiosorption and chemisorption measurements. The authors also wish to thank professor dr. K. Seshan for his assistance in the later stages of writing.

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