

Combination of autothermal reforming with water-gas-shift reaction—small-scale testing of different water-gas-shift catalysts

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Abstract

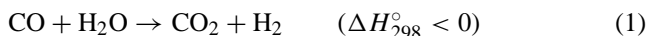
The amount of carbon monoxide in the reformat of the autothermal reforming (ATR) of liquid hydrocarbons can be significantly reduced by means of the water-gas-shift (WGS) reaction. It is possible to directly feed the reformat from the ATR of liquid hydrocarbons to the WGS reactor without deactivation of the WGS catalyst. In a first step, the dry reformat from the ATR and a separately fed stream of steam were used to conduct the WGS reaction. Special emphasis was given to the chemical composition of the reformat which under convenient reaction conditions did not feature any detrimental higher aliphatic or aromatic hydrocarbons. Applying these premises, no catalyst deactivation could be observed. Strong differences concerning the catalytic activity between the three investigated commercial monolithic catalysts could be observed. The most active one showed a very promising catalytic behaviour. At a gas hourly space velocity (GHSV) of $12,250 \text{ h}^{-1}$, CO conversion amounted to 85% at 280°C . This result reduces the CO concentration in the reformat from 6.1 to about 0.9 vol.%. In a second step, also the non-converted water from the ATR was fed to the reactor for the WGS reaction together with the additional components of the reformat. In this case, also the amount of total carbon dissolved in the water was analysed, which might—after adsorption—have a deleterious effect on the accessibility of the active sites of the WGS catalyst. No catalyst deactivation was observed within almost 90 h under ATR conditions generating only traces of carbon dissolved in the water.

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1. Introduction

An important requirement for the polymer electrolyte fuel cell (PEFC) is to deliver clean hydrogen (H_2) to its anode electrode, the kinetics of which are strongly decelerated by small amounts of carbon monoxide (CO). Within fuel processing, CO is produced in the upstream ATR of, for example, diesel fuel [1–3]. In [4], the upper limit for the concentration of CO entering the fuel cell anode is given as 0.005 vol.%. Therefore, it is essential to integrate several reaction units into the fuel cell system permitting a conspicuous reduction of the CO concentration in the gas mixture from ATR. A process step which helps to fulfil these demands is the heterogeneously catalysed water-gas-shift (WGS) reaction, which proceeds according to the following equation:



Grenoble and Estadt [5] investigated all transition metals from group VIII in the periodic table as well as Cu on different supports (Al_2O_3 , SiO_2 and C) for this reaction. They discovered that Cu is more active by a factor of 50 than the elements from group VIII. The authors ascribe this finding to the optimal adsorption heat of CO on Cu (about 80 kJ mol^{-1}). In their work, Rhodes et al. [6] describe the mode of operation of the industrial Cu-based catalyst for applications at low temperatures. The WGS reaction is well established in large steady-state operations such as hydrogen or ammonia plants. Cu is supported on ZnO and Al_2O_3 and encourages, on the one hand, the dissociative adsorption of H_2O , which leads to the formation of H_2 and an oxidised catalyst surface. The surface is reduced by adsorbing CO which is converted into CO_2 . This redox mechanism is characterised as regenerative. On the other hand, a so-called associative reaction pathway is discussed, in which on the Cu sites a formate species is formed from H_2O and CO which decomposes into H_2 and CO_2 . Wu and Saito [7] present a very stable Cu/ZnO/ Al_2O_3 catalyst which was doped with small amounts of SiO_2 . SiO_2 was found to inhibit the crystallisation of ZnO. Andreeva et al. [8] and

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Bocuzzi et al. [9] describe an Au/Al₂O₃ catalyst in their papers which is more active at reaction temperatures between 200 and 300 °C than the commercial Cu-based catalyst. A kinetic study of the WGS reaction on a Pt/MgO catalyst was performed by Wolf et al. [10]. They developed a very complex reaction scheme with five individual steps. CO₂ and H₂ adsorb on the MgO support whereas CO is bound to the Pt particles. These adsorption processes on both surfaces lead to the formation of several oxidised and reduced surface complexes which determine the reaction characteristics.

The challenges of an automotive application are fundamentally different from those of industrial use [11]. Wieland et al. [12,13] present a noble metal catalyst which was developed especially for automotive applications. The authors report that their catalyst does not require any in situ activation, it is non-pyrophoric and tolerant to temperature peaks. Furthermore, it can be coated on different substrates like foams, monoliths or metallic surfaces and therefore fulfils the basic requirements of a WGS catalyst for mobile applications. Baumann et al. report about the same catalyst that it does not undergo any methanation [14]. His group also performed kinetic measurements, which showed positive reaction orders for CO and H₂O but a slight inhibition by the partial pressures of CO₂ and H₂. With respect to mobile applications Baumann et al. [14] point out that with their catalyst a rapid start-up can be realised by injection of air into the reformat stream. H₂ and CO can be catalytically converted without any loss in activity for the WGS reaction. Balakos and Wagner from Süd-Chemie Inc. [15] stress the improved tolerance of their precious metal catalyst to condensation, poisons and oxidation, which might occur during numerous start-ups and shut-downs in mobile applications. Ruettinger et al. [16] from Engelhard Corp. emphasise very similar advantages of their new catalysts for the WGS reaction. They developed a base metal non-pyrophoric particulate catalyst with a very promising catalytic behaviour with respect to the requirements of fuel cell applications. This catalyst shows a very slight temperature increase of only 40 °C without any deactivation if accidentally exposed to air. Lost activity due to liquid water exposure can be regenerated in situ or ex situ. They also coated this material on monolithic substrates which can be operated at space velocities of 30,000 h⁻¹ at temperatures between 260 and 300 °C with only 1% CO in the product gas. Koryabkina et al. [17] determined kinetic parameters on different Cu-containing catalysts. This group found out that Cu is the active site for catalysis since the addition of CeO₂ and ZnO did not increase the rate per unit of Cu surface area. The results of their kinetic measurements indicate a strong inhibition of the forward reaction rate by the partial pressures of H₂ and CO₂. They present a redox mechanism with the reduction of surface oxygen by adsorbed CO as the rate-determining step. Swartz et al. [18] investigated a Pt/CeO₂ catalyst and figured out that it is non-pyrophoric and more active than commercial Cu-based catalysts at tem-

peratures above 250 °C. However, it shows significant deactivation rates caused by carbonaceous deposits. A deactivated Pt/CeO₂ catalyst can be regenerated by annealing in air.

Additionally, in [19,20], it is stated that a reactor for the WGS reaction in an automotive application should be cost-efficient, lightweight, tolerant of road vibrations and capable of rapid start-up. In [21], Krumpelt et al. go more into detail and specify target values. For transportation purposes small fuel cell systems in the range of 1–100 kW with a WGS reactor must not cost more than US\$ 100 kW⁻¹ to be economically viable. Furthermore, the US Department of Energy Office of Advanced Automotive Technologies (DOE/OAAT) postulates that in 2008 these systems must be able to undergo multiple start-ups and shut-downs, achieve maximum power from a cold start (–20 °C) in 1 min, respond to changes in the power demand from 10 to 90% in 1 s and have a power density of 800 W l⁻¹ [22]. To be able to meet these goals with respect to the WGS reactor three different commercially available catalyst-coated monoliths were applied in this work and tested concerning their catalytic activity. Their coating technique is already well established, they give rise to only slight pressure drops, they are easily adjustable to given power demands and their long use as DeNO_x catalysts has proven that they are very tolerant of road vibrations. A second focus of this work was the question of whether it is possible to directly combine the ATR of liquid hydrocarbons with the WGS reaction. In principle, it is conceivable that the WGS catalyst will be poisoned by impurities of the reformat coming from the ATR such as higher hydrocarbons, aromatics or other carbon-containing substances dissolved in the non-converted water from the ATR.

2. Experimental

The experiments with respect to the combination of ATR of liquid hydrocarbons with the WGS reaction were divided into two sections:

- (i) In the first section, a catalytic screening of three different commercial catalysts was performed with a dry reformat from the ATR (cf. Table 1), which contained as main components H₂, CO, CO₂, CH₄ and N₂ but

Table 1
Composition of the reformat in section (i)

	Concentration (vol.%)
CO	6.1
H ₂ O	23.5
H ₂	31.1
CO ₂	11.3
N ₂	27.6
CH ₄	0.1

no H₂O. H₂O was vaporised in an electrically heated furnace and separately fed to the reactor. The tests for the WGS reaction were performed in a reactor made of stainless steel (24 mm i.d.), in which the three different catalyst-coated monoliths (diameter: 21.5 mm; length: 95 mm; 93 cells per cm²) were centred. CO conversion as a function of reaction temperature was measured at three different GHSVs: approximately 12,250, 3100 and 1500 h⁻¹. The reformat was generated in a second reactor (28 mm i.d.) made of stainless steel, which contained a monolithic catalyst (diameter: 12 mm; length: 180 mm; 93 cells per cm²) from Umicore AG & Co. KG for the ATR of liquid hydrocarbons. The operation parameters were: $n(\text{H}_2\text{O})/n(\text{C}) = 1.80$ and $n(\text{O}_2)/n(\text{C}) = 0.44$ with a hydrocarbon feed of 45 g h⁻¹.

- (ii) In the second section, catalyst A from the screening in the first chapter (diameter: 21.5 mm; length: 95 mm; 93 cells per cm²) was chosen since it is a reasonably priced, non-pyrophoric base metal alternative to precious metal catalysts B and C from the screening. Therefore, it offers the most promising potential with respect to future marketable applications. It was placed in a reactor made of stainless steel (24 mm i.d.) and was examined at a GHSV of 11,600 h⁻¹ with a reformat from the ATR (cf. Table 3), which contained as main components H₂, CO, CO₂, CH₄, N₂ and H₂O. The reaction temperature at the end of the monolith was about 385 °C. This time the reformat was generated in a larger reactor (84 mm i.d.) made of stainless steel, which contained a monolithic catalyst (diameter: 50.8 mm; length: 85 mm; 93 cells per cm²) from Umicore AG & Co. KG for the ATR of liquid hydrocarbons. The operation parameters were: $n(\text{H}_2\text{O})/n(\text{C}) = 1.90$ and $n(\text{O}_2)/n(\text{C}) = 0.45$ with a hydrocarbon feed of 800 g h⁻¹. Only a partial stream of the reformat was fed to the WGS reactor.

In both sections, the different monolithic catalysts were insulated and fixed by a ceramic fleece. The hydrocarbon employed for the ATR experiments was a C₁₃–C₁₅ alkane mixture with a sulphur content of about 0.0001 vol.% and a boiling range between 235 and 265 °C.

In all experiments, the product gas was analysed by means of a mass spectrometer (Prima 600 S, VG Gas). The concentrations of the following gases were analysed: H₂, CO, CO₂, CH₄, N₂, O₂, C₂H₄, C₂H₆ and C₃H₆ (propene). Additional analyses of the dry product gas were carried out by GC/MS for the detection of C₂–C₇ hydrocarbons (capillary column: HP Plot-Q, 30 m length and 0.32 mm o.d.). Samples of non-converted H₂O (about 200 ml) coming from the ATR in section (ii) were condensed and collected directly behind the reactor. These samples were analysed for the dissolved amounts of total organic carbon and total carbon (performed according to DIN 38409 H3 by Institut Fresenius, Dortmund, Germany).

3. Results and discussion

3.1. Section (i)

In recent experiments concerning ATR of liquid hydrocarbons [1–3], convenient reaction conditions were found, under which no higher hydrocarbons (C₂–C₇) or aromatics in the dry reformat possibly deactivating the downstream WGS catalyst could be detected by means of GC/MS. Three different commercial WGS catalysts were compared with respect to their catalytic activity processing such a pure reformat. Table 1 summarises the composition of the reformat used in the comparison.

Fig. 1 shows strong differences between the WGS catalysts with respect to their catalytic behaviour at a GHSV of 12,250 h⁻¹. Sample C was much more active than catalysts A and B and reached thermodynamic equilibrium at about 280 °C with a CO conversion of 85–90%. At a reaction temperature of 225 °C CO conversion already amounted to approximately 40%. At reaction temperatures higher than 300 °C, CO conversion decreased due to thermodynamic limitations. This promising catalytic activity stands in contrast to that of catalysts A and B. In both cases, CO conversion amounted to less than 25% at reaction temperatures below 300 °C. The whole curves for CO conversion did not reach that on the basis of the thermodynamic equilibrium. CO conversion ran through a maximum of about 60% at 360 °C. When applying lower GHSVs of 3100 or 1500 h⁻¹ (cf. Figs. 2 and 3) very similar trends with respect to the CO conversion were observed. Again catalyst C showed by far the most promising catalytic activity and approached thermodynamic equilibrium at reaction temperatures plainly lower than 300 °C. In the case of a GHSV of 3100 h⁻¹, CO conversions of 88% at 248 °C and 42% at 203 °C were obtained. A GHSV of 1500 h⁻¹ resulted in remarkable CO conversions of 87% at 233 °C and even 71% at 202 °C. At these reaction temperatures, CO conversion of samples A and B only accounted for less than 40%.

From Fig. 1, a suitable operation temperature for the WGS reactor can be derived using catalyst C: 280 °C with a CO conversion of 85%. This means practically that at 280 °C CO concentration can be reduced from 6.1 to about 0.9 vol.% at a GHSV of 12,250 h⁻¹ operating with a practical reformer gas produced via ATR. Since 1 vol.% for CO is calculated to be the upper limit for the inlet concentration of the downstream reactor for the preferential oxidation of CO [23], a single WGS reactor within the fuel cell system operating with the above-described catalytic activity of sample C might be sufficient under the reaction conditions in Table 1. If a further reduction of the CO concentration to values lower than 0.9 vol.% in an additional low-temperature-shift reactor was necessary this reaction unit could be run with catalyst C at about 200 °C and a GHSV of 1500 h⁻¹. Under these conditions,

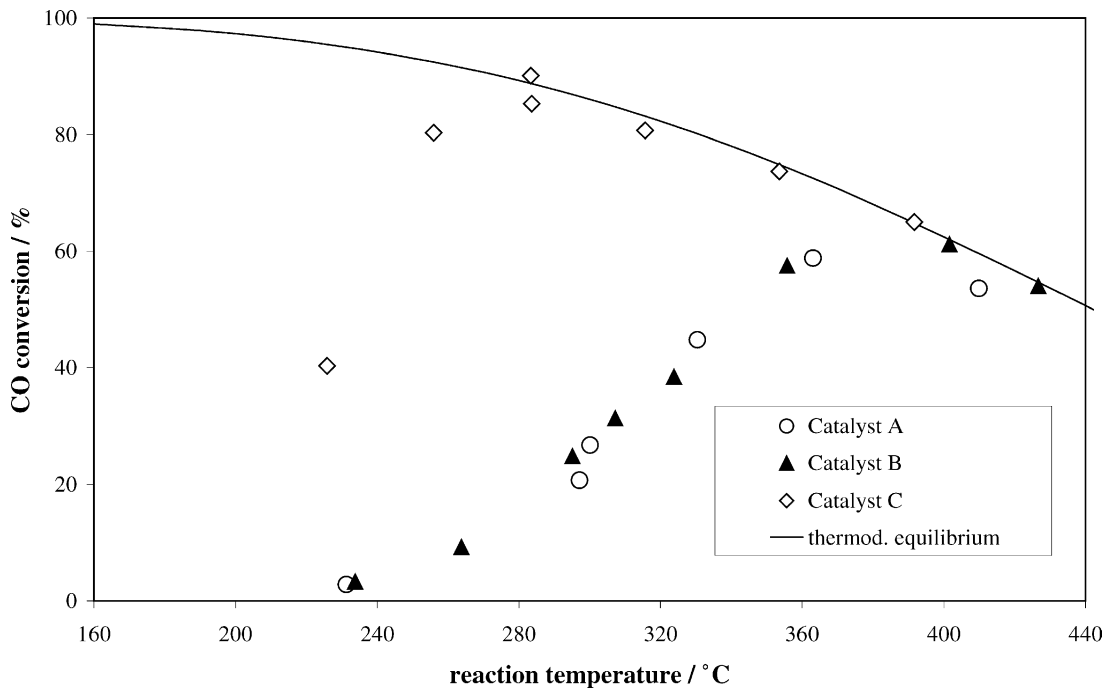


Fig. 1. CO conversion as a function of reaction temperature on three different commercial WGS catalysts. Reaction conditions given in Table 1; GHSV = 12,250 h⁻¹.

CO conversion amounted to 70% which would provoke a further reduction of the CO content from 0.9 to about 0.3 vol.%. No deactivation of any of the catalysts was observed.

3.2. Section (ii)

The motivation for the experiments in this section was to further investigate whether it is possible to directly feed the

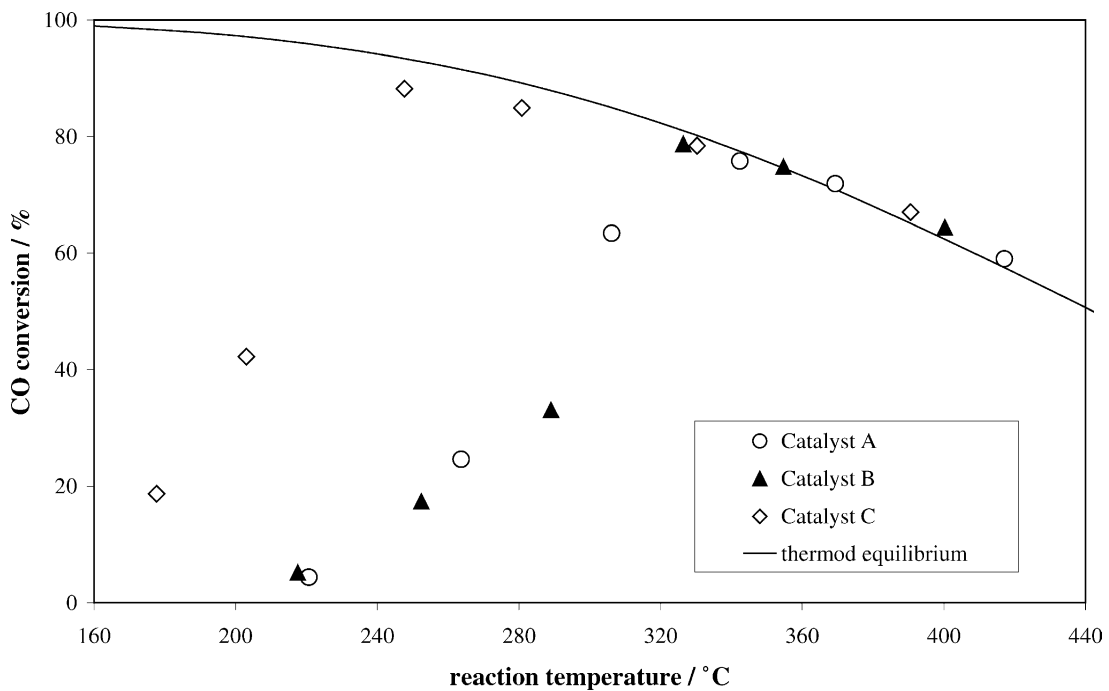


Fig. 2. CO conversion as a function of reaction temperature on three different commercial WGS catalysts. Reaction conditions given in Table 1; GHSV = 3100 h⁻¹.

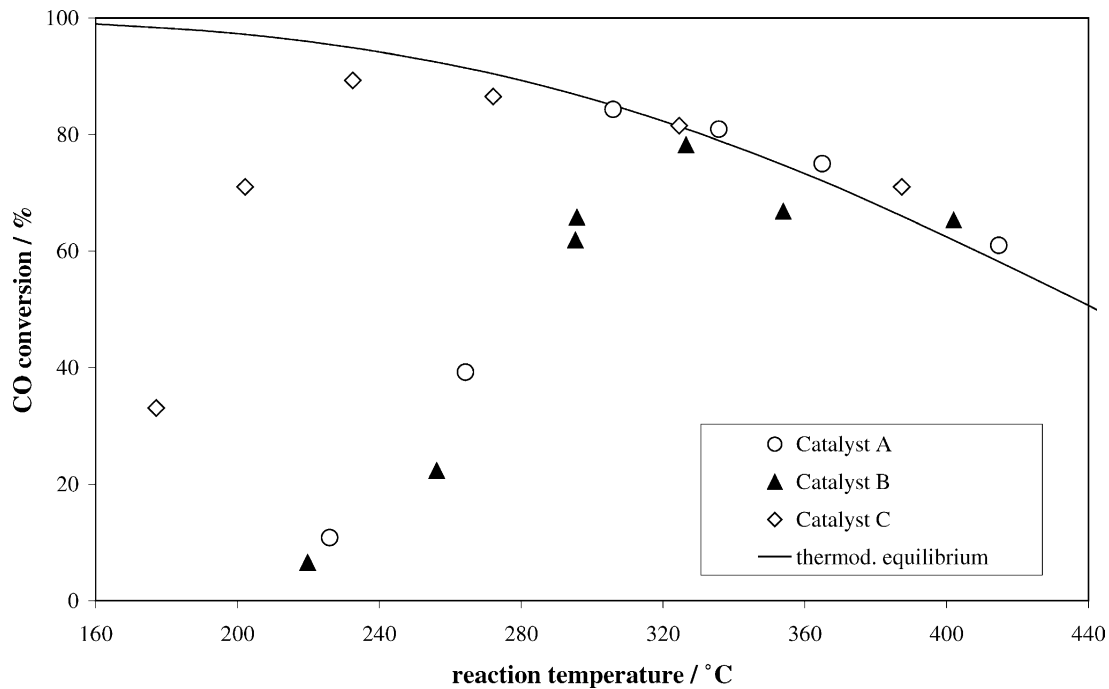


Fig. 3. CO conversion as a function of reaction temperature on three different commercial WGS catalysts. Reaction conditions given in Table 1; GHSV = 1500 h⁻¹.

water-containing reformat from the ATR to the WGS reactor after the results from section (i) had shown that there was no deactivation of the WGS catalyst by the dry reformat. Special emphasis is given to the influence of the water stream from the ATR on the long-term stability of the WGS catalyst.

Therefore, a set of analyses of the water streams from several ATR experiments previously described in [1] for the dissolved amounts of total organic carbon (TOC) and total carbon (TC) was conducted since these residues might poison the downstream WGS catalyst. The reaction conditions of the ATR experiments and the results of the analyses of the water are shown in Table 2.

Table 2 illustrates that the amount of total carbon dissolved in the water stream was always lowest in the case of experiments with an $n(\text{O}_2)/n(\text{C})$ ratio of 0.45. This is due

Table 2

Results of the analysis of the water stream coming from the ATR at different reaction conditions

Run	$m(\text{Hydrocarbon})$ (g h ⁻¹)	$n(\text{O}_2)/$ $n(\text{C})$	$n(\text{H}_2\text{O})/$ $n(\text{C})$	TOC (mg l ⁻¹)	TC (mg l ⁻¹)
1	600	0.41	1.9	73	78
2	800	0.45	1.7	17	22
3	800	0.45	1.9	16	21
4	800	0.41	1.9	44	49
5	600	0.45	1.9	16	20
6	800	0.41	1.7	120	125
7	600	0.41	1.7	96	100
8	600	0.45	1.7	24	27

ATR experiments in a random manner according to a 2³ factorial design.

to higher reaction temperatures within the monolith, which were always found in the case of higher partial pressures of oxygen [1]. There was almost no influence of the hydrocarbon feed and the $n(\text{H}_2\text{O})/n(\text{C})$ ratio. Therefore, the conditions from run 3 were chosen for the combination with the WGS reactor because a low amount of TC was observed and a high water stream was applied. Furthermore, the GC/MS analysis under the reaction conditions from run 3 evidenced that there were no higher hydrocarbons in the dry reformat which might also deactivate the downstream WGS catalyst. Table 3 gives the composition of the reformat generated during run 3. Fig. 4 shows the temperature at the inlet of the WGS reactor and at three different positions in the axial direction of the monolith as a function of time on stream. Catalyst A was chosen for this experiment.

CO conversion at the outlet of the reactor was constant during the whole experiment and measured to be 54%. This value is plainly lower than that based upon thermodynamics related to the reaction temperature at $x = 80$ mm (385 °C),

Table 3

Composition of the reformat in section (ii)

	Concentration (vol.%)
CO	8.6
H ₂ O	22.7
H ₂	28.5
CO ₂	9.5
N ₂	30.1
CH ₄	0.2

Conditions according to run 3 in Table 2.

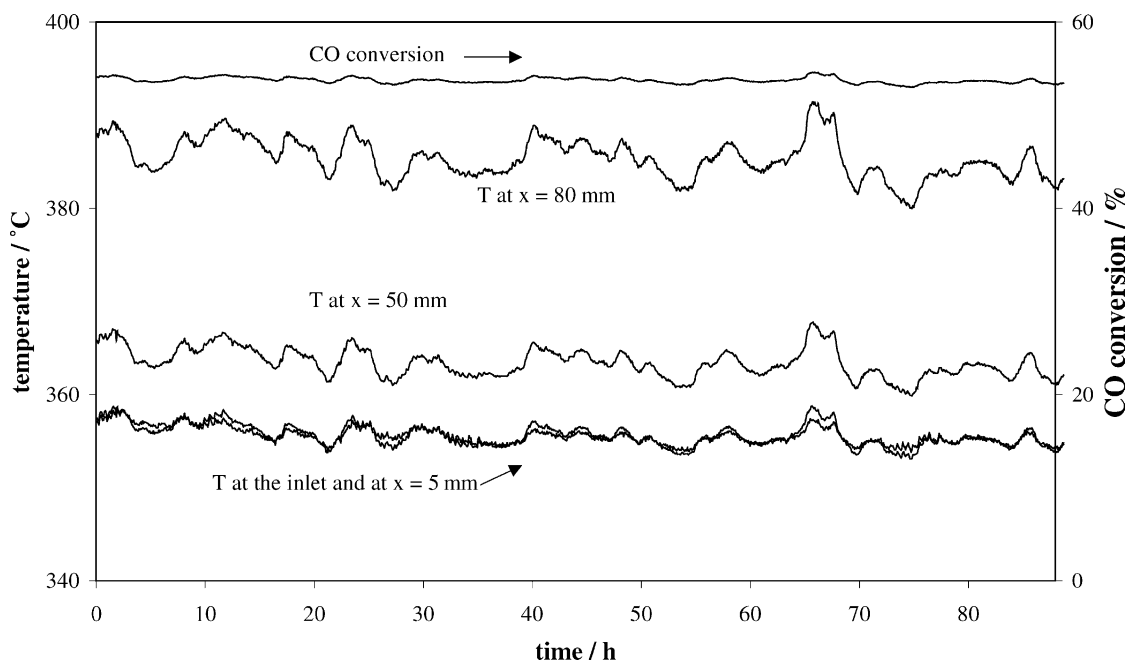


Fig. 4. Temperature at different positions in the axial direction with catalyst A and CO conversion as a function of time on stream. Reaction conditions given in Table 3; $X(\text{CO}) = 54\%$; $\text{GHSV} = 11,600 \text{ h}^{-1}$.

which was calculated to be approximately 70%. Under these conditions, the reaction is kinetically controlled. Fig. 4 underlines the fact that due to the exothermicity of the WGS reaction the reaction temperature obviously increased in the axial direction of the monolith from about 355 to 385 °C. This finding shows that the reaction proceeded along the whole length of the monolith and not only in the upper part as was observed in the case of the partial oxidation of liquid hydrocarbons [1–3]. However, the most important result which can be drawn from Fig. 4 is that no deactivation of the WGS catalyst could be observed within almost 90 h since the temperature at each of the three positions and CO conversion remained constant.

4. Conclusions

The amount of carbon monoxide in the reformat of the ATR of liquid hydrocarbons can be significantly reduced by means of the WGS reaction. It is possible to directly feed the reformat from the ATR of liquid hydrocarbons to the WGS reactor without deactivation of the WGS catalyst.

In a first step, the dry reformat from the ATR and a separately fed stream of steam were used to conduct the WGS reaction. Special emphasis was given to the chemical composition of the reformat, which under convenient reaction conditions did not feature any detrimental higher aliphatic or aromatic hydrocarbons. Applying these premises, no catalyst deactivation could be observed. Strong differences concerning the catalytic activity between the three investigated com-

mercial monolithic catalysts could be observed. The most active one showed a very promising catalytic behaviour. At a GHSV of $12,250 \text{ h}^{-1}$, CO conversion amounted to 85% at 280 °C. This result reduces the CO concentration in the reformat from 6.1 to about 0.9 vol.%. If a further decrease of the CO content is necessary it can be performed at lower reaction temperature, e.g. at about 200 °C and a GHSV of 1500 h^{-1} . This low-temperature-shift reactor can achieve an additional diminution of the CO concentration from 0.9 to about 0.3 vol.%. However, the rather low value for the GHSV would diminish the practical impact of this additional step since the reactor would become larger by a factor of four in comparison to the reaction unit run at 280 °C and $12,250 \text{ h}^{-1}$.

In a second step, also the non-converted water from the ATR was fed to the reactor for the WGS reaction together with the additional components of the reformat. In this case, also the amount of total carbon dissolved in the water was analysed, which might — after adsorption — have a deleterious effect on the accessibility of the active sites of the WGS catalyst. No catalyst deactivation was observed within almost 90 h under ATR conditions generating only traces of carbon dissolved in the water.

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