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Highly selective methanation by the use of a microchannel reactor

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Abstract

The successful application of a microchannel reactor to reduce the CO content by methanation in a model gas mixture containing CO, CO_2, O_2 and H_2 can be shown. Microchannels coated with a Ru/SiO_2 and a Ru/Al_2O_3 catalyst were used at standard residence times of about 300 ms. The methanation allowed to remove CO almost completely from the gas flow at a temperature of 300 °C using a Ru/SiO_2 catalyst. Although oxygen was added to the feed, the CH_4-selectivity was still 95% at temperatures of 350 °C using the Ru/SiO_2 catalyst.

It can be shown, that the CO conversion is higher at temperatures between 140 and 200 °C under oxidizing conditions because CO can be converted to CO_2. For temperatures from 200 to 320 °C the amount of oxidized H_2 increases more than the amount of oxidized CO and consumes most of the O_2. In parallel, CO methanation is increasing temporarily up to 250 °C with increasing temperature maybe due to formation of Ru^{n+} sites so that the CH_4 space time yield by CO methanation is also higher than that by CO_2 methanation. At temperatures between 250 and 300 °C a local minimum in methane formation from CO methanation is determined which might be attributed to a considerable decrease in Ru^{n+} sites by oxygen consumption. The CH_4 space time yield by CO methanation clearly decreases with H_2O co-feed compared to the same conditions but without water over the reaction temperature range examined.

If CO (in a mixture of CO and CO_2) has to be converted over a Ru/SiO_2-catalyst by methanation a sufficient amount of O_2 has to be added and temperature has to be controlled precisely. Because of the inner dimensions and the enhanced heat transfer coefficients of the microchannel reactor the latter demand can be met very easily. Temperature ranges can be controlled precisely, which is important to maximize the ratio of CH_4 space time yield by CO to CO_2 methanation.

The experiments demonstrate that the microchannel reactor is an excellent tool for studying the reaction network of methanation of CO in presence of oxygen, CO_2 and hydrogen without heat transfer limitation.

Keywords: Microreactor; Microchannels; Methanation; Ruthenium; Silica; CH_4-selectivity

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1. Introduction

In the past, methanation has received considerable attention for natural gas substitution. The substitution process involves the partial oxidation of coal to CO and subsequent recombination of CO with H_2 to form methane [1]. The methanation reaction is also commonly applicable in ammonia plants to remove carbon oxides from inlet streams which otherwise poison the ammonia synthesis catalyst. In the present, selective methanation became also attractive in order to reduce the CO content to less than 100 ppm in hydrogen-rich reforming gases for fuel cell applications [2,3]. Polymer electrolyte fuel cells (H_2-PEMFC) do not tolerate CO concentrations of more than 100 ppm. Until now microreactors were not used for selective methanation, but similar reactions, e.g. the selective oxidation of CO were already examined in microreactors [4]. Whenever selective processes are needed and selectivity can be affected by hot spots, a microchannel reactor should help to increase process efficiency due to enhanced heat transfer from or to the catalyst.

Methanation is a highly exothermic, reversible reaction in accordance with the following main reaction equation:

$$3H_2 + CO \leftrightharpoons CH_4 + H_2O,$$
$$\Delta H_R(T = 523\,K) = -217\,kJ\,mol^{-1} \qquad (1)$$

In presence of O_2, a possible component in product gases of partial oxidation or autothermal reforming processes, the following side reactions can occur:

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$$2CO + O_2 \leftrightharpoons 2CO_2, \quad \Delta H_R(T = 523\,K) = -288\,kJ\,mol^{-1} \quad (2)$$

$$2H_2 + O_2 \leftrightharpoons 2H_2O, \quad \Delta H_R(T = 523\,K) = -247\,kJ\,mol^{-1} \quad (3)$$

In all reforming processes CO_2 is present that can also react to methane by the following pathway (Sabatier reaction):

$$4H_2 + CO_2 \leftrightharpoons CH_4 + 2H_2O, \quad \Delta H_R(T = 523\,K) = -189\,kJ\,mol^{-1} \quad (4)$$

Another alternative to reduce the CO amount in a reforming product gas is the water gas shift reaction due to the presence of water vapor:

$$H_2O + CO \leftrightharpoons CO_2 + H_2, \Delta H_R(T = 523\,K) = -41\,kJ\,mol^{-1} \quad (5)$$

Numerous supported precious metal catalysts were investigated for CO removal by selective methanation in literature:

Ni/Al_2O_3-catalysts that were prepared by Aksoylu et al. [5] showed CO conversions of more than 90% and CH_4-selectivities of more than 60%. However, longer residence times were needed for full conversion on these Ni-catalysts. This leads us to the assumption that nickel catalysts are not suitable for microreactors, although Xavier et al. [1] were able to increase the activity of Ni/Al_2O_3-catalysts by doping Al_2O_3 with 1.5 wt.% CeO_2.

The role of the catalyst support was examined by Lin et al. [6]. They showed that the activation energy of H_2 adsorption was affected by the electron modification of the ruthenium due to the interactions between metal and support. The activation energy decreases in the order of $Ru/TiO_2 > Ru/Al_2O_3 > Ru/SiO_2$.

Utaka et al. [7] examined the reaction of a simulated reforming gas over Pt-catalysts. At temperatures from 100 to 250 °C high CO conversions of more than 90% were reached, but most of the conversion was caused by the water gas shift reaction. They mentioned, that the highest conversions were reached at SiO_2 and Al_2O_3-supports impregnated with ruthenium.

Aßmann et al. [8] determined that it is necessary to have O_2 in the gas mixture to oxidize the Ru^0 sites to Ru^{n+} sites. Only these sites, which are preferably formed under oxidizing conditions at lower temperatures, are capable to adsorb large amounts of CO and are necessary for the methanation.

Fujita et al. [9] examined the competitive methanation without oxygen co-feed (10 vol.% CO and 10 vol.% CO_2 in 90 vol.% H_2) at 1 bar over Ru/SiO_2 and other catalysts. They determined that CO_2 methanation rate at 200 °C is 4.6 times faster than the CO methanation rate.

Over et al. [10] pointed out that changing the CO/CO_2 ratio in the gas feed to higher values than 2:1 will deteriorate the overall activity due to blocking the surface by CO molecules.

In the present study the results of the selective methanation will be presented for two catalysts, namely Ru/Al_2O_3 and Ru/SiO_2. The gas mixture corresponds to the typical composition behind a reformer combined with a high temperature water gas shift reactor. These catalysts have been successfully applied to microstructured metal foils. The coated foils were stacked in a clamping device and tested for selectivity and conversion.

2. Experimental

2.1. Microchannel reactor

The microchannel reactor consists of 27 stainless steel foils with etched microchannels and a clamping device (Fig. 1). The foils were coated with the catalysts on the microstructured side and were subsequently stacked in a clamping device. The etched foils and the clamping device are forming the microchannel reactor (Fig. 2). Because the heat production of the chemical reactions was very small and heat capacity and heat conductivity of the whole microstructure is very high only the reaction passage with in- and outlet connection of the reactor was necessary. The two other connections of the reactor normally used for a cooling passage were closed. The geometric data of the microstructured foils and hence of the microstructured foil stack are given in Table 1. In Fig. 2, two SEM pictures show a coated microstructured foil and the face of the foil stack. The geometric surface of a foil includes the top of the fin, the channel bottom and the channel walls. By clamping of the foils, the geometric inner surface of the foil stack includes the channel walls, the bottom and the top of the channels. The coated surface of the stack includes only the walls and the bottom of the channels as the back sides of the foils are not coated.

2.2. Catalyst preparation

Because other catalyst preparation methods are not applicable to completely manufactured microchannel reactors, it was decided to use a two step catalyst preparation method: sol–gel followed by wet impregnation. The porous oxide layers of alumina and silica were prepared via the sol–gel method as described by Haas-Santo et al. [11]. Aluminium-sec-butylate

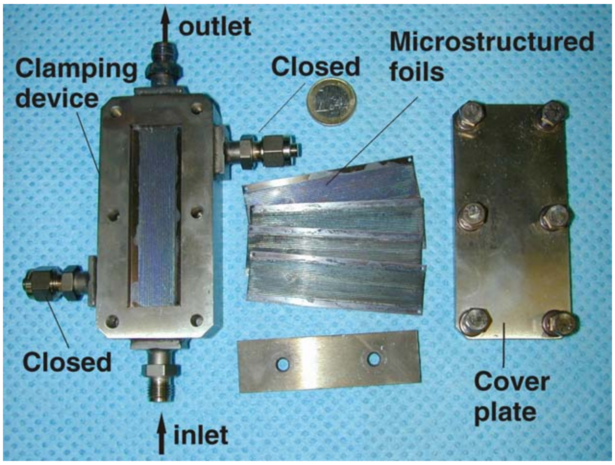

Fig. 1. Microchannel reactor for methanation experiments with clamping device and coated foils.

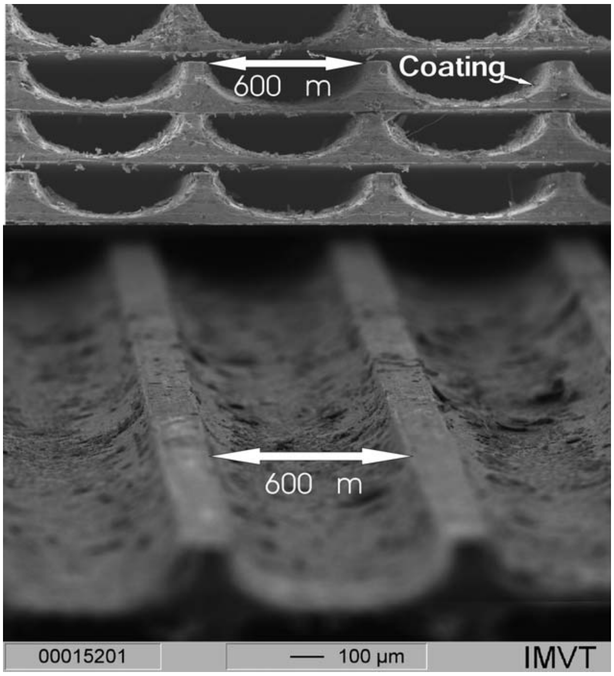

Fig. 2. SEM of a microstructured foil coated with Ru/SiO_2 and stacked foils.

(AISB, Fluka) and tetraethylorthosilan (TEOS, FLUKA) were used as precursor, acetylacetonate as stabilizer, nitric acid as catalyst and ethanol as solvent. The walls of the microchannels were coated with the gel equivalent of 81.6 mg Al_2O_3 and 32.1 mg SiO_2. The coated foils were dried first for 3 h at 90 °C. Subsequently, the coated foils were heated to the final calcination temperature of 500 °C. By weighing before and after the coating procedure a mass increase of 85.3 and 33.5 mg was observed, which is 5% more than expected by the weight of the coating. This can be explained by the oxidation of the metal substrate. After 3 h of calcination, the coating of all foils was impregnated with 5 ml (Al_2O_3-coated foils) and 10 ml (SiO_2-coated foils) of aqueous $RuCl_3$ (Sigma–Aldrich) solution containing 13 g/l Ru. Drying of the impregnated samples was carried out at 90 °C for 3 h. For a second time the coated foils were heated to a calcination temperature of 500 °C with a calcination time of 3 h. The mass increases then were reasonable with respect to the theoretically expected values. The solution volume and the Ru-content applied for impregnation corresponded to 65 mg Ru at Al_2O_3 (81.6 mg) and 130 mg Ru at SiO_2 (32.1 mg).

2.3. Catalyst characterization

The adhesion of the catalysts on the substrate surface was also examined by weighing. The mass of the coated foils before and after the reaction experiments were determined. No mass loss was observed although pressure oscillations were applied to the samples during the experiments by turning on and off the gas flow using a fast switching valve.

Laterally ground sections were prepared with the catalyst-coated foils embedded for determination of the layer thickness by scanning electron microscopy (SEM).

The catalyst mass per geometric surface area (1525 mm^2) of one microstructured foil, calculated compositions, and thickness of the catalyst layers estimated from SEM are listed in Table 2.

The structure of the catalyst layer components were examined by X-ray diffraction (XRD) from the top side of the foils. A Siemens D5005 diffractometer using a copper target at 40 kV × 40 mA and a scanning speed of $1^\circ\ min^{-1}$ was used therefore. The catalyst morphology was determined by scanning electron microscopy with the same samples.

Fig. 3 clearly shows cracks in the Ru/Al_2O_3-catalyst layer, which are a result from the shrinking of the Al_2O_3 applied to stainless steel during calcination.

In contrast to the Al_2O_3-layer, the SiO_2-layer exhibits smaller cracks (Fig. 4). Ru-particles and Ru-whiskers can be recognized especially in the cracks of the SiO_2-layer.

Beside the reflexes of stainless steel present below the catalyst layer, the XRD-analysis of both catalysts shows elementary Ru (hexagonal). The Ru/Al_2O_3-catalyst shows reflexes of Al_2O_3 (hexagonal). SiO_2 in the Ru/SiO_2 catalyst seems to be amorphous.

The surface area of the foil-catalyst system was determined by adsorption measurements with nitrogen. Values of the specific surface area are given as the surface enlargement ratio of a layer (see Table 2):

$$\text{enlargement ratio} = \text{BET} - \text{surface} : \text{geometric surface of foil} \quad (6)$$

The BET-surface was determined by means of an Autosorb 1C adsorption facility using a U-shaped flow reactor. Therefore the catalyst coated microstructured foils were coated in small pieces. By heating at 393 K under vacuum, humidity and other volatile substances were removed from the catalyst samples to be investigated. The surface area covered by N_2 (BET surface) and the mean pore diameter were determined by pressure variation. The results are presented in Table 2.

It was impossible to determine the active Ruthenium surface by chemisorption experiments. The ratio of catalyst to metal foil is very small so that the Ruthenium surface area is below the detection limit of the Autosorb 1C adsorption facility.

Table 1
Geometric data of the microsstructured foils and of the foil stack

Channel width	600 µm	Channels per foil	17	Number of foils	27
Channel height	150 µm	Length of foil	78 mm	Height of stack	6.2 mm
Fin width	150 µm	Width of foil	20 mm	Channel volume of stack	3222 mm^3
		Geometric surface of one foil	1535 mm^2	Coated surface of stack	27167 mm^2

Table 2
Substrate, specific mass, composition, surface enlargement and mean pore diameter of the catalysts applied to the microstructured foils

Catalyst	Substrate	Catalyst mass/coated surface of stack (mg/cm^2)	Composition	Surface enlargement ratio ($m^2\ m^{-2}$)	Mean pore diameter (nm)	Layer thickness (μm)
Ru/Al_2O_3	Stainless steel	0.54	55.7% Al_2O_3	526	7	0.5–2
Ru/SiO_2	Stainless steel	0.60	19.8% SiO_2	470	7	0.5–2

2.4. Test rig

The scheme of the test rig is shown in [4]. Mass flow controllers (MKS) were used for dosing the model gas components. The water used for the experiments testing the H_2O influence on methanation was fed by a HPLC pump (Knauer) into a steel capillary. This capillary was heated by a resistance wire and water was subjected to evaporation. Water vapor and the gases N_2 and O_2 were premixed. In heated pipes, this gas mixture was heated to the temperature desired. In a micromixer that was also heated by a resistance wire, CO and H_2 were added to the N_2/O_2/steam-mixture. The model gas then entered the microreactor with the catalytically coated microstructured foils via an insulated connection pipe. The microreactor was also heated electrically using a resistance wire. For temperature control, three thermocouples were installed. In the model gas flow, a first thermocouple measured the temperature between the micromixer and the microstructured reactor ($T_{R,in}$). A second thermocouple measured the gas outlet temperature downstream of the microreactor ($T_{R,out}$). In addition, the temperature of the housing $T_{housing}$ was measured. In all experiments the difference between the measured three temperatures was below 1 K. From worst case estimation a maximum reaction heat of 25 W (complete H_2-oxidation and CO-methanation) was calculated, so that isothermal conditions are ensured. Moreover, the heat losses through the reactor metal body were so high during the experiments, that it was necessary to heat the reactor electrically to equilibrate these heat losses. The pressure drop of the microreactor was negligible. After temperature equilibration, the inlet volume fractions of O_2, H_2, CO, H_2O and N_2 (corresponding to the bypass concentrations) and the product volume fractions were determined by means of a gas chromatograph (Agilent 6890N). Conversion and selectivities of the reaction were determined from changes of inlet to outlet concentration. Before the first measurement every catalyst was treated about 10 h under reaction condition (1 vol.% O_2; 1 vol.% CO; 25 vol.% H_2; 25 vol.% H_2O; 48 vol.% N_2; $T = 350\ ^\circ C$) to simulate an aging and to ensure stable catalyst performance.

The following experimental conditions were used for performing the methanation experiments.

The total inlet gas flow $\dot{V}_{in}$ measured by the mass flow controllers was varied between 0.22 and 0.66 l/min (STP). The end mass flow $\dot{V}_{end}$ can be calculated in two kinds:

$$\dot{V}_{end} = \frac{[N_2]_{in}}{[N_2]_{end}}\dot{V}_{in} = \frac{[CO_2]_{in} + [CO]_{in}}{[CO]_{end} + [CO_2]_{end} + [CH_4]_{end}}\dot{V}_{in} \quad (7)$$

The temperature range was from 100 to 380 °C. A mixture of 25 vol.% H_2, 1 vol.% CO, and 1 vol.% O_2 and 73 vol.% N_2 was applied to the catalyst at three standardized residence times τ (177, 251 and 474 ms at 250 °C) of the gas mixture in the microchannel volume ($V_R = 3222\ mm^3$), keeping into account that the catalyst layer having a average thickness of 1 μm:

$$\tau = \frac{V_R}{\dot{V}} \quad (8)$$

From the measured inlet concentrations $[CO]_{in}$ and end concentrations $[CO]_{end}$ and $[H_2O]_{end}$ and $[CH_4]_{end}$ (all indicated in the unit of mol l^{-1}), the conversion $X(CO)$ can be determined:

$$X(CO) = \frac{[CO]_{in} - [CO]_{end}(\dot{V}_{end}/\dot{V}_{in})}{[CO]_{in}} \quad (9)$$

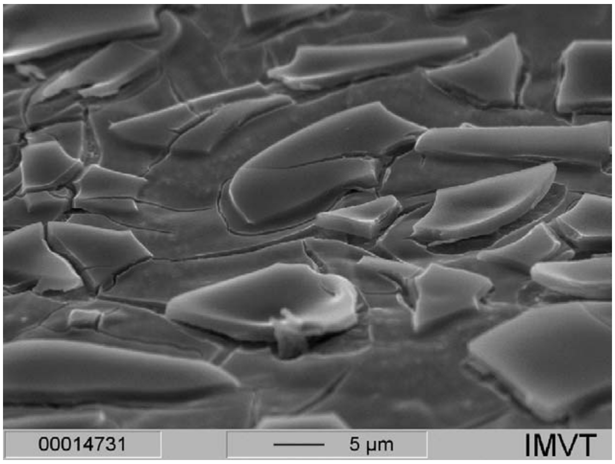

Fig. 3. SEM of the Ru/Al_2O_3 catalyst on a microstructured stainless steel foil.

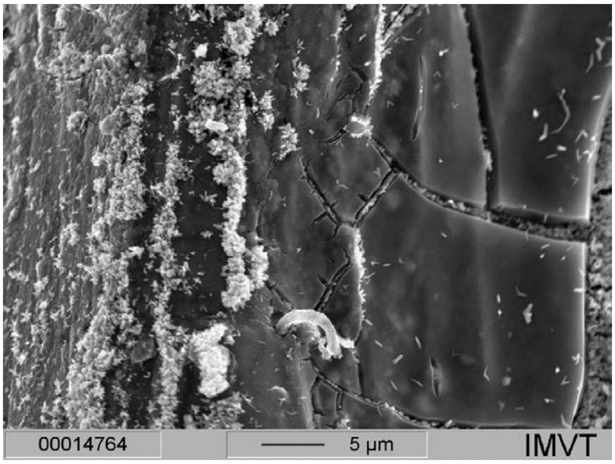

Fig. 4. SEM of the Ru/SiO_2 catalyst on a microstructured stainless steel foil.

The CH_4 selectivity $S(CH_4)$ and CO_2 selectivity $S(CO_2)$ can be expressed as follows:

$$S(\mathrm{CH_4}) = \frac{[\mathrm{CH_4}]_{\mathrm{end}}(\dot{V}_{\mathrm{end}}/\dot{V}_{\mathrm{in}})}{[\mathrm{CO}]_{\mathrm{in}} - [\mathrm{CO}]_{\mathrm{end}}(\dot{V}_{\mathrm{end}}/\dot{V}_{\mathrm{in}})},$$

$$S(\mathrm{CO_2}) = \frac{[\mathrm{CO_2}]_{\mathrm{end}}(\dot{V}_{\mathrm{end}}/\dot{V}_{\mathrm{in}})}{[\mathrm{CO}]_{\mathrm{in}} - [\mathrm{CO}]_{\mathrm{end}}(\dot{V}_{\mathrm{end}}/\dot{V}_{\mathrm{in}})} \tag{10}$$

To validate the values of $X(CO)$, $S(CH_4)$ and $S(CO_2)$ for every measured point, a carbon balance was calculated. There were no hints for carbon deposition.

To examine the influence of water vapor, 20 vol.% steam were added. Additional experiments were performed where some amount of N_2 was replaced by CO_2 (1.5–6 vol.%) to study the competitive methanation of CO and CO_2.

The CH_4 space time yield STY is an interesting value which can be referred to certain variables characterizing the reaction system. With the reactor channel volume the CH_4 space time yield is defined as follows [12]:

$$\mathrm{STY} = \frac{1}{V_{\mathrm{R}}}\frac{\Delta n_{\mathrm{CH_4}}}{\tau}\left[\frac{\mathrm{mol}}{1\,\mathrm{h}}\right] \tag{12}$$

The definition of the amount of converted CO per channel volume ($X(CO)_V$) corresponds to the CH_4 space time yield when no CO_2 or O_2 is added to the feed:

$$X(\mathrm{CO})_{\mathrm{V}} = \frac{1}{V_{\mathrm{R}}}\cdot\frac{\Delta n_{\mathrm{CO}}}{\tau}\left[\frac{\mathrm{mol}}{1\,\mathrm{h}}\right] \tag{13}$$

3. Experimental results

3.1. Comparison of the catalysts

The CO-conversions plotted as a function of reaction temperature for the two catalysts tested reveal that the Ru/SiO_2-catalyst has the higher activity at low temperature (Fig. 5). At 285 °C and 177 ms standard residence time, the CO-conversion reaches a maximum value of 95%. The Ru/Al_2O_3-catalyst reaches that value of CO-conversion only at 360 °C. The difference between the CH_4-selectivities is considerably. The Ru/SiO_2-catalyst exhibits its highest CH_4-selectivity of only 82% at a temperature of 305 °C, whereas a selectivity of 99% is reached by the Ru/Al_2O_3-catalyst at 340 °C. Analysis of the product gas revealed that CO, not reacting to CH_4 was converted into CO_2 by total oxidation (Eq. (2)). Up to a temperature of 140 °C O_2 is completely converted to CO_2 and H_2O according to Eqs. (2) and (3). At shorter and longer residence times (not shown here) the Ru/SiO_2-catalyst also exhibits a better performance than the Ru/Al_2O_3-catalyst regarding CO conversion and CH_4 selectivity.

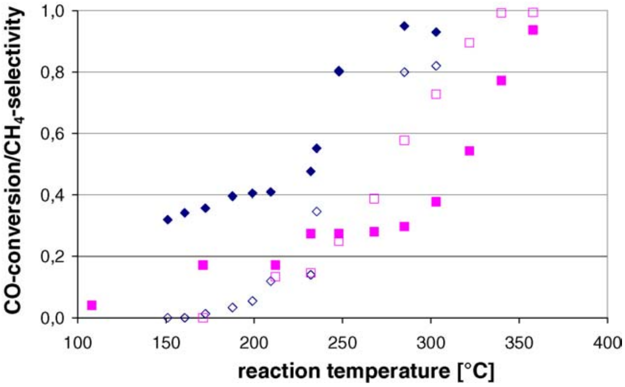

Fig. 5. CO conversion and CH_4-selectivities of the methanation as a function of temperature for the two catalysts ((◆) $X(CO)$ for Ru/SiO_2; (■) $X(CO)$ for Ru/Al_2O_3; (◇) $S(CH_4)$ for Ru/SiO_2 (□) $S(CH_4)$ for Ru/Al_2O_3). Standard residence time of 177 ms. Inlet composition of model gas: $[CO]_{in} = [O_2]_{in} = 1$ vol.%; $[H_2]_{in} = 25$ vol.%; $[N_2] = 73$ vol.%.

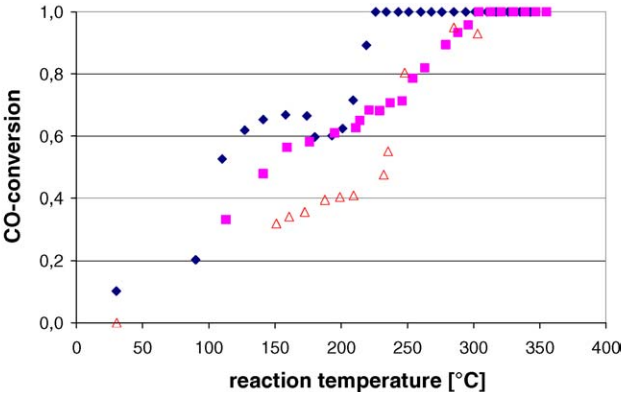

Fig. 6. CO conversion at Ru/SiO_2 of the methanation as a function of temperature for three standard residence times: (◆) 474 ms; (■) 251 ms; (△) 177 ms. Inlet composition of the model gas: $[CO]_{in} = [O_2]_{in} = 1$ vol.%; $[H_2]_{in} = 25$ vol.%; $[N_2] = 73$ vol.%.

3.2. Variation of the residence time

Plotting the CO-conversion for the Ru/SiO_2-catalyst as a function of the reaction temperature for three standard residence times, an expected higher conversion can be observed with longer residence times (Fig. 6); that means complete conversion is reached at lower temperatures for longer residence times. Fortunately, also the CH_4-selectivities are elevated with increasing residence times (Fig. 7). The sum of

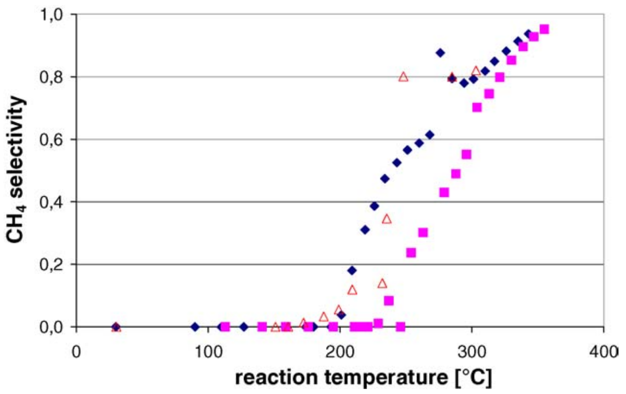

Fig. 7. CH_4 selectivity at Ru/SiO_2 of the methanation as a function of temperature for three standard residence times: (◆) 474 ms; (■) 251 ms; (△) 177 ms. Inlet composition of the model gas: $[CO]_{in} = [O_2]_{in} = 1$ vol.%; $[H_2]_{in} = 25$ vol.%; $[N_2] = 73$ vol.%.

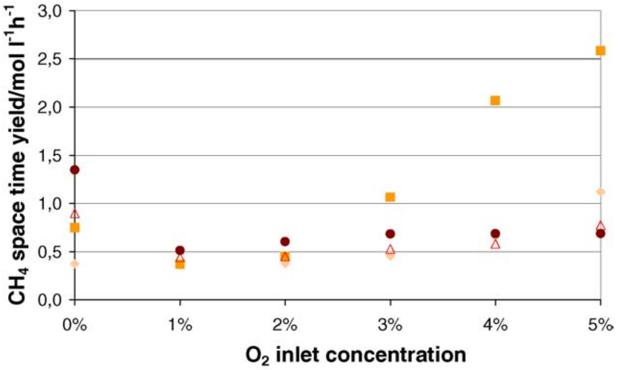

Fig. 8. CH_4 space time yield at Ru/SiO_2 of the CO-methanation as a function of the O_2 inlet concentration for four temperatures (◆) 237 °C; (■) 265 °C; (△) 294 °C; (●) 309 °C; inlet composition of the model gas: $[CO]_{in} = 1$ vol.%; $[H_2]_{in} = 25$ vol.%; $[N_2] = 69–74$ vol.%.

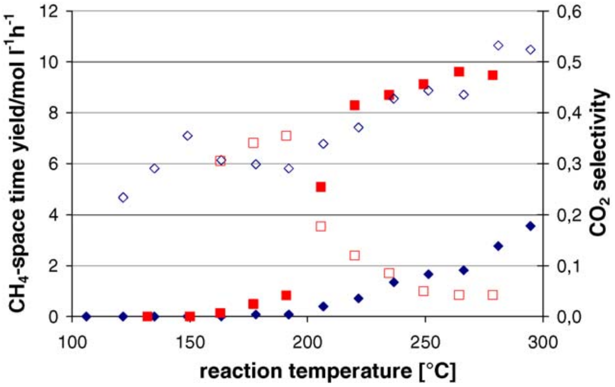

Fig. 9. Comparison of the CH_4 space time yield at Ru/SiO_2 of the methanation with and without water tested at a standard residence time of 177 ms; inlet gas composition ($[N_2]$. balance): (◆) STY (CH_4); (◇) $S(CO_2)$ for: $[CO]_{in} = [O_2]_{in} = 1$ vol.%; $[H_2]_{in} = 25$ vol.%; $[H_2O]_{in} = 20$ vol.%; (■) STY (CH_4) (□) $S(CO_2)$ for: $[CO]_{in} = [O_2]_{in} = 1$ vol.%; $[H_2]_{in} = 25$ vol.%; $[H_2O]_{in} = 0$ vol.%.

the methane selectivity and the CO_2-selectivity was always 100%.

The conversion plot at a residence time of 474 ms shows evidence of a maximum at 170 °C. Additionally it is remarkable that at a residence time of 474 ms the methane selectivity curve shows a first maximum at 280 °C (Fig. 7). This selectivity maximum reveals that in this point the mechanism of the methane formation changes. The maximum was reproduced several time, it was not time-dependent and was always occurring at a temperature that is characteristic for the particular residence time. It was furthermore independent of the direction of the temperature ramp, i.e. if the temperature was de- or increased. As for each measuring point it was waited until equilibration of the reactor was reached an in-stationary phenomena can be excluded.

3.3. Variation of O_2 inlet concentration

Plotting the CH_4 space time yield for the Ru/SiO_2-catalyst as a function of the O_2 inlet concentrations for four reaction temperatures, a STY decrease from 0 to 1 vol.% O_2 (Fig. 8) can be observed. At higher O_2 concentrations the CH_4 space time yields rises for all four temperatures with increasing O_2 inlet concentrations. The largest rise can be noticed at a temperature of 265 °C.

The experiments with an inlet O_2 concentration of 5 vol.% show the highest distribution of the CH_4 space time yield values, the experiments with an inlet O_2 concentration of 1 vol.% reveal the smallest distribution at the different temperatures.

3.4. Influence of water

Fig. 9 shows the CH_4 space time yield and the CO_2 selectivities for a model gas mixture with and without water co-feed for the Ru/SiO_2 catalyst. It can be demonstrated that the CH_4 space time yield of a gas mixture without H_2O is much higher compared to the CH_4 space time yield for a gas mixture with 20 vol.% H_2O. The CH_4 space time yield of the experiment without water co-feed shows an S-shaped curve, the one with H_2O exhibits a constantly rising curve. At higher temperatures above 200 °C the increasing CO_2 selectivities of the water containing gas mixture show, that the water gas shift reaction takes place.

3.5. Competitive methanation of CO and CO_2

To test the competitive methanation of CO and CO_2, experiments were performed with Ru/SiO_2 and different CO_2 contents. As shown in Fig. 10, the CH_4 space time yields increase with rising temperature for all gas mixtures. The gas mixture containing no CO_2 and only 1 vol.% CO exhibits the highest CH_4 space time yield for temperatures below 240 °C. The gas mixture that contains 4.5 vol.% CO_2 but no CO reveals the highest CH_4 space time yield at temperatures from 250 to 300 °C. The gas mixture with 4.5 vol.% CO_2 and 1 vol.% CO exhibits the lowest CH_4 space time yield in the entire temperature range.

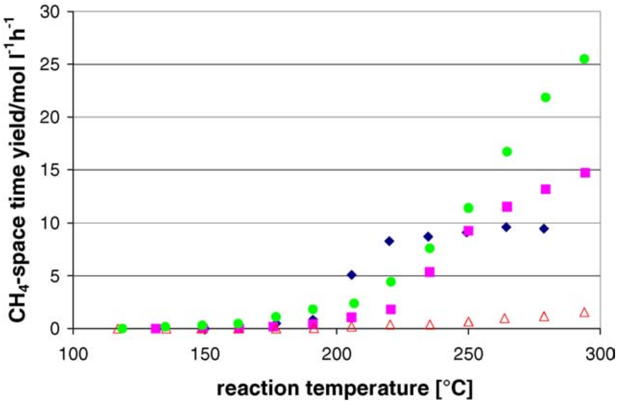

Fig. 10. Comparison of the CH_4 space time yield at Ru/SiO_2 of the methanation with different CO_2 contents tested at a standard residence time of 177 ms. Inlet gas composition ($[N_2]$: balance): (◆): $[CO]_{in} = 1$ vol.%; $[CO_2]_{in} = 0$ vol.%; $[O_2] = 1$ vol.%; $[H_2] = 25$ vol.%; (■): $[CO]_{in} = 1$ vol.%; $[CO_2]_{in} = 1.5$ vol.%; $[O_2] = 1$ vol.%; $[H_2] = 25$ vol.%; (△): $[CO]_{in} = 1$ vol.%; $[CO_2]_{in} = 4.5$ vol.%; $[O_2] = 1$ vol.%; $[H_2] = 25$ vol.% (●): $[CO]_{in} = 0$ vol.%; $[CO_2]_{in} = 4.5$ vol.%; $[O_2] = 1$ vol.%; $[H_2] = 25$ vol.%;.

To compare the CO-oxidation (Eqs. (2) and (4)) CH_4 space time yield by CO_2 methanation with the CH_4 space time yield by CO-methanation, each of these reactions were conducted separately. The results of these experiments are summarized in Fig. 12.

By comparing the CH_4 space time yield from CO with the amount of converted CO per volume and the Sabatier reaction (Eq. (4)) rate, some interesting relations can be observed. The CH_4 space time yields of the CO_2-methanation (Fig. 11: ●, ■) rise strongly with increasing temperatures. For temperatures below 260 °C the CO_2-methanation reaction in the gas mixture containing 1 vol.% O_2 (Fig. 11: ●) is obviously slower than without O_2 (Fig. 11: ■). The converted CO per volume without hydrogen addition, i.e. only CO oxidation (Fig. 11: △) rises with increasing temperatures until complete conversion at 200 °C is reached. The CH_4 space time yield by CO methanation with addition of 1 vol.% O_2 to the gas mixture (Fig. 11: ◆) exhibits a faster rising between 200 and 250 °C compared to the similar experiment of CO_2 methanation (Fig. 11: ●). Above 250 °C the STY of CO methanation (Fig. 11: ◆) remains constant for a CO-conversion of more than 99% and a CH_4-selectivity >98%.

4. Discussion and conclusion

A Ru/Al_2O_3 and Ru/SiO_2 catalyst were successfully applied to microreactors to reduce the CO content by methanation in a model gas mixture that contains the major product components of a natural gas reformer or of a partial oxidizer used for hydrogen production. At temperatures below 300 °C Ru/SiO_2 showed higher CO conversion and higher selectivity than the Ru/Al_2O_3.

At standard residence times of about 300 ms, the methanation allowed to remove CO almost completely from the gas flow at temperatures of 300 °C using a Ru/SiO_2 catalyst. However, the maximum CH_4-selectivity of 99% was reached at a temperature of 350 °C using a Ru/Al_2O_3 catalyst and oxygen addition to the feed.

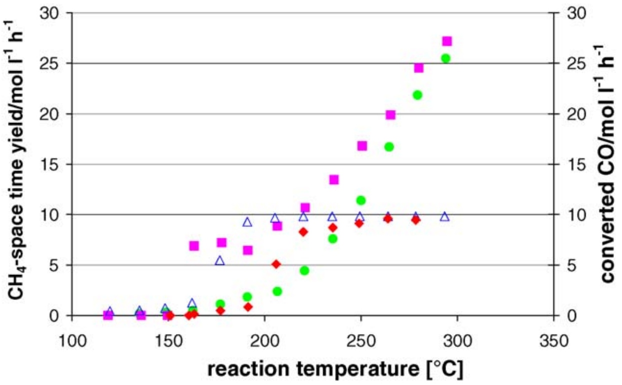

Fig. 11. CH_4 space time yield by CO_2 methanation; inlet gas composition: (●): $[CO_2]_{in} = 4.5$ vol.%; $[O_2]_{in} = 1$ vol.%; $[H_2]_{in} = 25$ vol.%; $[N_2]$: balance (■): $[CO_2]_{in} = 4.5$ vol.%; $[O_2]_{in} = 0$ vol.%; $[H_2]_{in} = 25$ vol.%; $[N_2]$: balance CH_4 space time yield by CO methanation; inlet gas composition: (◆) $[CO]_{in} = 1$ - vol.%; $[O_2]_{in} = 1$ vol.%; $[H_2]_{in} = 25$ vol.%; $[N_2]$: balance converted CO per volume and time; inlet gas composition: (△) $[CO]_{in} = 1$ vol.%; $[O_2]_{in} = 1$ vol.%; $[H_2]_{in} = 0$ vol.%); $[N_2]$: balance all experiments performed at a standard residence time of 177 ms.

For all catalysts the CH_4 selectivity curve versus temperature showed unsteadiness at around 250 °C when adding oxygen to the feed. This unsteadiness reveals that at this temperature the mechanism of the methane formation changes. Two competitive reaction take place, firstly the CO methanation, secondly the CO oxidation. The large increase in CO conversion and CH_4 selectivity at 220 °C ($\tau = 474$ ms) and 250 °C ($\tau = 177$ ms) can be explained by the initiation of the CO methanation.

Concerning only the CO methanation it would show the typical S-shape of an reaction. However, there is a competitiveness of CO methanation with CO_2 methanation and the CH_4 space time yield from CO methanation is higher only at temperatures between 200 and 250 °C. Above 250 °C CO_2 methanation dominates.

At temperatures between 200 and 250 °C we determined that the H_2 oxidation gets faster than the CO oxidation reaction and consumes most of the O_2. Since more CO is available for CH_4 formation, the CH_4-selectivity i.e. the CO methanation space time yield rises considerably. At temperatures above 250 °C the methane selectivity decreases temporarily. Following the observations of Aßmann [10] the amount of Ru^{n+} sites could be assumed to decrease considerably due to consumption of all oxygen by water formation from H_2. This assumption can be supported by the fact that CO_2 methanation gets faster than CO methanation above 250 °C. However, a simpler hypothesis is that the activation energy of the CO methanation is higher than of the CO_2 methanation and that the reaction rate of the CO methanation is accelerated by O_2 whereas the reaction rate of the CO_2 methanation is slowed down by O_2. The influence of Ru^{n+} sites has to be proven with suitable spectroscopic methods.

Above 250 °C the CH_4 space time yield increases for both reactions i.e. the CO and the CO_2 methanation and a considerable amount of CO_2 will be converted.

Over the whole reaction temperature range examined the CO methanation rate clearly decreases with a co-feed of H_2O compared to the methanation rate for the same conditions but without water. This is probably because H_2O is competing for active sites at the catalyst surface and above 200 °C also a part of CO in a gas mixture containing 25 vol.% H_2O is converted by the water gas shift reaction into CO_2.

If CO (in a mixture of CO and CO_2) has to be converted over a Ru/SiO_2-catalyst by methanation a sufficient amount of O_2 has to be added and temperature has to be controlled precisely according to the selectivity behaviour determined in the present study. Because of the inner dimensions and the enhanced heat transfer coefficients of the microreactor systems the latter demand can be met very easily. Temperature ranges can be controlled precisely, which is important for further application, i.e. to maximize the ratio of CO to CO_2 methanation rate. For practical applications the reaction heat of exothermal reactions like CO and H_2-oxidation can be distributed for activation of the reaction sites more efficiently in the microchannel system compared to conventional reactors [7]. This enables shorter space time yields. In conventional reactors phenomena like the maximum of CO conversion (Figs. 5 and 6) can be further missed due to temperature gradients. The received data can be used additionally for kinetic studies because they are trustworthy according to the measured temperatures.

We think that the microchannel reactor is an excellent tool for studying the reaction network of methanation of CO in presence of oxygen, CO_2 and hydrogen without heat transfer limitation.

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