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Production of hydrogen by short contact time partial oxidation and oxidative steam reforming of propane

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Abstract

Partial oxidation (POX) and oxidative steam reforming (OSR) of propane have been studied over Rh-impregnated alumina foams in the short contact time regime. The experiments were performed over a wide temperature range (300–1000 °C) at close to atmospheric pressure. It was found that a furnace temperature of 700 °C is optimal for the production of hydrogen for both reactions (POX and OSR) in this system. Variations in the total flow rate revealed an effect of residence time on the product distribution during both POX and OSR. The production of hydrogen was hardly affected by the residence time, but an influence of the residence time on the selectivity to all other products was observed. Hydrocarbon byproducts were increasingly formed at shorter residence times while formation of partial and complete oxidation products increased with longer residence times. The Rh foam catalyst also showed promising stability under strong oxidation conditions.

Keywords: Propane; Hydrogen; Partial oxidation; Oxidative steam reforming

1. Introduction

Hydrogen is at present mainly used for production of ammonia and methanol, in oil refineries and in hydrogenations in the chemical industry. Hydrogen is furthermore considered an attractive energy carrier for the future, to be used as a clean fuel in combustion engines and fuel cells. However, because it does not exist as hydrogen gas in nature, it has to be produced from water, hydrocarbons or other hydrogen containing compounds. Due to the low volumetric density and molecular size, there are severe technical challenges associated with the storage and distribution of hydrogen in an energy system. While solutions to these challenges are worked out, an interesting alternative is to generate hydrogen from a suitable hydrogen carrier on the spot where it is to be used.

At present, the most energy efficient and economical way of producing hydrogen is via large-scale steam and/or autothermal reforming of hydrocarbons, in particular methane. Non-catalytic partial oxidation of heavy oils and coal are also important methods used industrially. Hydrogen may also be produced by electrolysis of water, providing a product with high purity, but usually associated with high cost.

Propane is a possible fuel for distributed or small-scale production of hydrogen in Norway. It is produced in large quantities from natural gas and associated gas in the oil industry. Norway with its low population density has almost no natural gas infrastructure. Propane, being liquid at approximately 9 bar, is easily stored and distributed. Catalytic partial oxidation (POX) and oxidative steam reforming (OSR) are possible routes for the conversion of propane to hydrogen. Reactions involving oxygen are fast and potentially more efficient than conventional steam reforming. An additional advantage of these processes is the possibility to run under autothermal conditions [1].

Oxidation reactions are often so fast that the reaction takes place on or near the external surface of the catalyst. In such situations, external mass transfer becomes significant in controlling reaction rates and thereby the selectivity of the

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catalyst [2,3]. It is therefore important to facilitate both the migration of reactant through the boundary layer to the surface and the removal of intermediates from the surface through the boundary layer into the bulk [4].

The production of hydrogen by oxidation reactions can be performed in the short contact time regime. Short contact time reactors hold the promise of greatly reducing the reactor volume, and therefore smaller reactors (or higher throughput) can be achieved. Short contact times can be reached by using structured catalytic systems where the catalytically active materials are deposited on structured ceramic or metallic substrates [5,6]. This group of structured catalysts includes monolithic catalysts with honeycomb structure, ceramic foams, corrugated-plate catalysts with cross-flow or parallel channels as well as metallic gauzes, and some have already been applied in important industrial processes [7–11]. Partial oxidation [4,12–24] and oxidative dehydrogenation of light hydrocarbons [25–30] are among the most studied short contact time reactions. Partial oxidation of methane has been studied using metal oxide catalyst systems [22,31] and noble-metals [4,12,14,19–24,31]. Rhodium has been found to be superior to platinum with respect to optimising H_2 and minimising H_2O formation [14,15,31,32]. The Rh catalyst showed no loss in activity at 1000 °C for several hours [31]. Nickel catalysts offered similar conversion and selectivity, but showed a stronger tendency to deactivation [31].

In this study, Rh-impregnated alumina foams have been tested for catalytic partial oxidation and oxidative steam reforming of propane as potential high-throughput, structured catalysts for hydrogen or synthesis gas production. Such foams exhibit low density, and a permeable structure of cells with high surface-to-volume ratio as well as high strength-to-weight ratio. The POX and OSR experiments were performed over a wide temperature range, and comparisons were made between the Rh/Al_2O_3 foam and an equivalent unimpregnated Al_2O_3 foam. The effect of residence time was studied by increasing the total flow rate, and preliminary stability tests were performed. Moreover, POX and OSR were compared with respect to the production of hydrogen. The pressure of the reaction is maintained at a value slightly higher than atmospheric pressure by a needle valve in order to enable gas sampling to the analysis system. The sensitivity of experimental results to small variations in this overpressure has also been explored.

2. Experimental

2.1. Rh structured catalysts

Extruded alumina foams of 84% porosity (ε) were supplied by Goodfellow and cut into cylindrical pieces (15 mm o.d., 12.7 mm length). A 3 mm opening was cut along the middle axis to allow for temperature measurements within the foam. The foams were impregnated by a $Rh(NO_3)_3{\cdot}2H_2O$ solution, followed by drying at 100 °C for 1 h and calcination in flowing air at 600 °C for 4 h. Reduction was performed in situ at 700 °C for 1 h in a flow of hydrogen prior to the experiments. The impregnation was performed in order to obtain a final loading of Rh of about 0.01 wt.% as estimated by the solution uptake. The Rh/Al_2O_3 foam was placed between two inert cordierite (400 cells/in.^{2}) pieces in a quartz reactor (15 mm i.d., 7 mm length).

2.2. Experimental set-up

Continuous flow experiments were carried out over Rh/Al_2O_3 or unimpregnated Al_2O_3 foams at close to atmospheric pressure and furnace temperatures in the range 300–800 °C. The active Rh foam was inserted into a quartz tube between the two pieces of cordierite and enclosed in a gold insulated furnace (Thermcraft Trans Temp), which becomes transparent at high temperatures. A thermocouple was placed inside a 3 mm quartz tube and inserted into the stack of cordierite and alumina foam. A similar experimental set-up has been described in more detail previously [30].

The reactant gas mixture consisted of propane, air and nitrogen in the case of partial oxidation of propane, for which a C/O ratio of 0.8 was chosen as an optimum ratio according to reported values [27]. Steam was added to the feed gas when oxidative steam reforming was performed, and the C/O ratio was then lowered to 0.5 as a precaution to coke formation. The H_2O/O_2 ratio of 2 was chosen in order to feed equal amounts of H_2O and O_2 in terms of O-content [33]. The concentration of propane in the feed gas and the total flow rate were the same for both types of reaction. In experiments with varying residence time, the total flow rate was changed while the feed gas composition was kept constant. An air-cooled, cross-flow microstructured heat exchanger, designed and built by the Forschungszentrum Karlsruhe GmbH [34], was installed after the reactor for water removal from the product stream. As mentioned, a slight overpressure on the main stream was applied to maintain a side-stream for sampling. The dry samples were analysed by gas chromatography (Agilent G2891A MicroGC).

The selectivity to hydrogen ($S(H_2)$) was calculated according to the following equation:

$$S(H_2) = \frac{F_{\text{tot,out}}}{F_{\text{tot,in}}} \frac{C_{H_2,\text{out}}}{4C_{C_3H_8}X_{C_3H_8,\text{in}}} \quad (1)$$

where $F_{\text{tot,in}}$ and $F_{\text{tot,out}}$ are total volumetric gas flows at reactor inlet and outlet, respectively, expressed in N ml/min at STP (0 °C, 1 bar), $C_{H_2,\text{out}}$ the concentration of hydrogen in the outlet gas, $C_{C_3H_8,\text{in}}$ the concentration of propane in the feed gas and $X_{C_3H_8}$ is the conversion of propane. It should be noted that this selectivity quantifies how much hydrogen is obtained relative to the amount of propane converted, irrespective of whether steam has been added to the reactant mixture or not. The residence time (τ) was calculated as the ratio of void volume of Al_2O_3 foam to the total volumetric gas flow at reactor inlet ($F_{\mathrm{tot,in}}$) as follows:

$$\tau = \frac{\varepsilon V_{\mathrm{Al_2O_3\,foam}}}{F_{\mathrm{tot,in}}} \tag{2}$$

The calculation of void volume of the foam was based on the porosity of the Al_2O_3 foam (ε) and the overall volume of the alumina foam piece ($V_{\mathrm{Al_2O_3\,foam}}$).

3. Results and discussion

3.1. Effect of temperature

The conversion of reactants and the selectivity to main products obtained during partial oxidation and oxidative steam reforming of propane over 0.01 wt.% Rh/Al_2O_3 are shown as a function of the furnace temperature in Fig. 1A and B, respectively. In both cases, the conversion of propane reached 80% already at a furnace temperature of 400 °C. The conversion of oxygen was nearly complete or complete for both reactions at temperatures above 400 °C. The temperatures measured inside the reactor/catalyst were, however, much higher as shown in Fig. 2A (POX) and B (OSR). The difference between furnace and reactor temperatures varied from 430 °C at the lowest to 167 °C at the highest furnace temperature during partial oxidation (Fig. 2A). Ignition was observed during slow heating of the reactor from 300 to 400 °C for POX. The ignition was accompanied by strong heat generation causing the maximum reactor temperature to reach 830 °C already at a furnace temperature of 400 °C. Differences between reactor and furnace temperatures were also present during oxidative steam reforming varying from 345 to 154 °C upon increasing the furnace temperature from 400 to 800 °C (Fig. 2B).

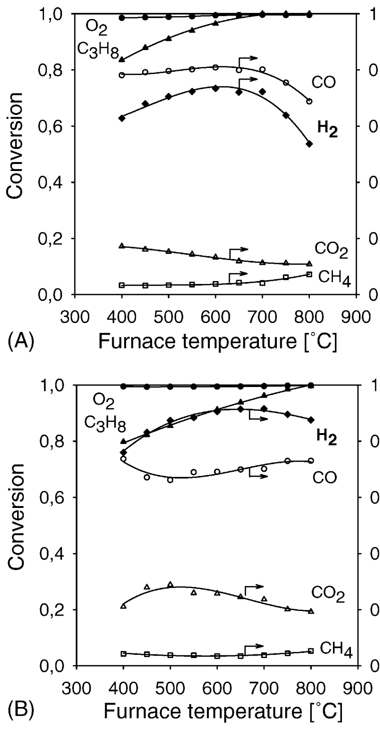

Fig. 1. Conversion of propane and oxygen and selectivity to main products as a function of furnace temperature for partial oxidation of propane (A) and oxidative steam reforming of propane (B) over 0.01 wt.% Rh/Al_2O_3 foam. Total flow rate: 1000 N ml/min. (A) Feed flows (N ml/min): C_3H_8 (101), O_2 (190), and N_2 (709). (B) Feed flows (N ml/min): C_3H_8 (100), O_2 (150), N_2 (450), and H_2O (300).

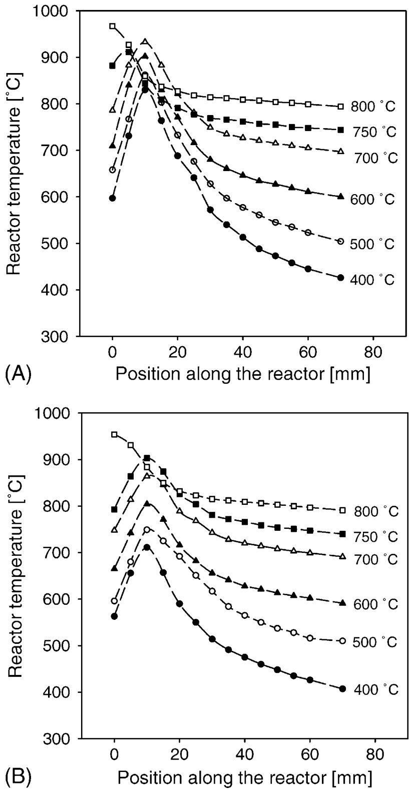

Fig. 2. Temperature profiles taken during POX (A) and OSR of propane (B) over 0.01 wt.% Rh/ Al_2O_3 foam. Conditions as in Fig. 1.

Fig. 2A and B also provides information about the axial position of the maximum temperature, i.e. the hot-spots were the exothermic oxidation takes place. For both reaction types, the point of maximum reactor temperature was located in the middle of the active monolithic piece at furnace temperatures less than 700 °C. At 750 °C, the hot-spot moved in direction of the inlet of the active monolithic piece in the POX experiment. At 800 °C, the temperature profile is dramatically changed and the hot-spot is located somewhere within the inert cordierite monolithic piece placed in front of the active catalyst. In the case of OSR, the temperature profile and the hot-spot position are almost identical to what was observed for POX although the transition appears more abrupt for OSR above 750 °C. However, at 800 °C the maximum temperature is located in the cordierite in front of the Rh foam catalyst also for OSR. Shifting of the hot-spot location could also be observed visually, since the furnace is transparent at these temperatures.

The shift of the maximum temperature position along the reactor was also observed during experiments with the unimpregnated Al_2O_3 foam. At temperatures of 750 °C or higher, the temperature profiles and maximum reactor temperatures were similar to those of the Rh/Al_2O_3 foams, whereas at lower temperatures, there were significant differences between the temperature profiles. The above-mentioned similarity was found for both partial oxidation and oxidative steam reforming conditions. These observations indicate that gas phase ignition of the reaction mixture occurs at such high temperatures, and that the process undergoes a transition to a mode where homogeneous reactions are more dominant. Thus, the contribution from gas phase reactions needs to be considered when interpreting results at sufficiently high temperatures during short contact time POX and OSR.

The hydrogen selectivity increased with increasing furnace temperature until 700 °C, and then decreased. This was observed for both partial oxidation (Fig. 1A) and oxidative steam reforming (Fig. 1B). The yield of hydrogen relative to propane converted was remarkably higher during oxidative steam reforming. Fig. 1A and B also shows that carbon monoxide is a main product. In the case of POX, the selectivity reaches 80% whereas a selectivity of about 70% is obtained during OSR. Carbon monoxide can be converted to hydrogen in one or two consecutive water-gas shift reaction steps when hydrogen is the desired product.

The product gas mixture after partial oxidation and oxidative steam reforming also contains hydrocarbons such as methane, ethene, ethane, propene, and at certain conditions ethyne and traces of C_{4+} compounds. The selectivity to methane is <7% for POX and <6% for OSR (Fig. 1A and B). The selectivity to ethene obtained during POX and OSR is even lower; <4 and <2%, respectively. Ethane and propene were detected in the product stream as well, with ethane selectivities always below 0.3% and propene selectivities always below 0.9% for both POX and OSR. Finally, ethyne was formed during both POX and OSR, but at the highest temperatures only. The highest selectivity to ethyne obtained during OSR was noticeably lower (0.05% at 800 °C) than during POX (8.5% at 800 °C). Ethyne could not be detected at furnace temperatures below 650 and 700 °C for POX and OSR, respectively. Higher hydrocarbons, mainly C_5 and C_7 hydrocarbons, were detected in trace amounts at the highest temperatures during both POX and OSR.

The optimal temperature for POX and OSR of propane is the temperature at which the highest yield of hydrogen and the lowest production of byproducts can be obtained. During these experiments, the highest hydrogen production was obtained at a furnace temperature of 700 °C for OSR as well as for POX. In case of OSR, a furnace temperature of 700 °C corresponded to a maximum temperature inside the reactor of 864 °C. In case of POX, the maximum temperature was 933 °C for a furnace temperature of 700 °C. This temperature was also low enough to avoid formation of most of the higher hydrocarbons. A furnace temperature of 700 °C was therefore chosen as a starting point for parameter studies and preliminary stability tests/deactivation studies.

The experiments performed with unimpregnated Al_2O_3 foams give insight into contributions from gas-phase reactions. Gas-phase reactions were initiated above a furnace temperature of 650 °C in case of POX (Fig. 3A) and above 550 °C for OSR (Fig. 4A). After a sharp increase in the conversion of propane and oxygen over a relatively narrow furnace temperature interval, propane and oxygen conversion was complete at 850 °C for POX and almost complete at the same temperature for OSR. In both types of reaction, carbon dioxide was a main product at lower temperatures (Figs. 3B and 4B), and the selectivity to carbon dioxide was much higher as compared to the Rh/Al_2O_3 foam (Fig. 1A and B). The selectivity to hydrocarbons (C_2H_2, C_2H_4, C_2H_6, and C_3H_6) showed in Figs. 3A and 4B was remarkably higher than over Rh/Al_2O_3. Moreover, C_{4+} hydrocarbons were detected during these blank experiments, whereas formation of higher hydrocarbons was suppressed when using the Rh/Al_2O_3 catalyst. The selectivity to hydrogen and carbon monoxide increased with temperature but were not as high as with Rh/Al_2O_3.

Since homogeneous reactions may play a role even when the Rh catalyst is used, it is worth looking in detail into conversion and selectivity for both blank and Rh-catalyzed

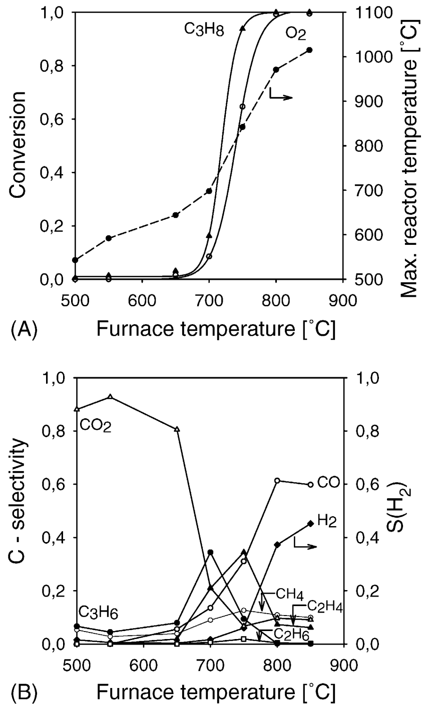

Fig. 3. Conversion of oxygen and propane (A), C-selectivity and selectivity to hydrogen (B) as a function of the furnace temperature during partial oxidation of propane over the unimpregnated Al_2O_3 foam. Total flow rate: 1000 N ml/min; feed flows (N ml/min): C_3H_8 (101), O_2 (190), and N_2 (709).

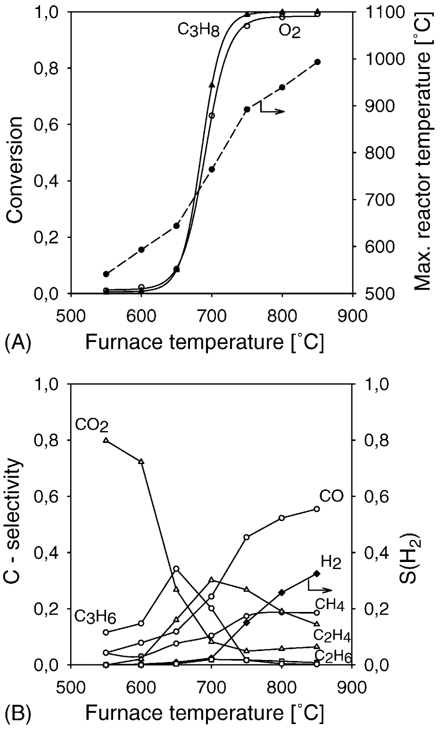

Fig. 4. Conversion of oxygen and propane (A), C-selectivity and selectivity to hydrogen (B) as a function of the furnace temperature during oxidative steam reforming of propane over unimpregnated Al_2O_3 foam. Total flow rate: 1000 N ml/min. Feed flows (N ml/min): C_3H_8 (100), O_2 (150), N_2 (450), and H_2O (300).

experiments. To be able to compare these experiments, the maximum reactor temperature was taken as a reference point. A maximum temperature of 933 °C was observed during POX over the Rh catalyst when experiments were performed at 700 °C (Table 1). The blank experiment with the closest maximum temperature (971 °C) corresponds to the experiment performed at a furnace temperature of 800 °C. Since homogenous reactions are a main issue, the blank experiment with higher maximum reactor temperature was chosen for comparison. Even if the conversion of propane and oxygen was almost complete in both cases, the selectivity to hydrogen and carbon monoxide is substantially higher when the Rh catalyst was applied. The similar tendencies could be found also for OSR (Table 1). Much higher selectivity to hydrogen and carbon monoxide was obtained over Rh/Al_2O_3 than over Al_2O_3. Thus, heterogeneous reactions taking place on the Rh particles are the main contributions to the formation of hydrogen and carbon monoxide. Nevertheless, contributions from homogenous reactions cannot be excluded and they become increasingly important with temperature.

3.2. *Effect of residence time*

A variation of the total flow rate from 1000 to 2000 N ml/min corresponds to a change in residence time from 0.105 to 0.053 s. The main influence was on the conversion of oxygen which increased with increasing residence time (lower total flow rate) during partial oxidation (Fig. 5A) as well as during oxidative steam reforming (Fig. 5B). The conversion of propane was only slightly affected by the variation of the total flow rate.

For partial oxidation of propane (Fig. 5A), the selectivity to carbon monoxide and hydrogen as well as to carbon dioxide and water undergoes a slight increase with residence time. Accordingly, the selectivity to all hydrocarbons except ethyne decreases with residence time. During POX, the selectivity to ethyne displays a maximum at a total flow rate of 1400 N ml/min flow rate corresponding to a residence time of 0.075 s. According to these results, one may presume that the highest concentrations of hydrocarbons can be found near the inlet of the active monolithic substrate, i.e. at extremely short residence times. Thus, maximum hydrocarbon formation can be expected at residence times below the range studied, i.e. at 0.05 s or lower with the exception of ethyne (Fig. 5A). Since the selectivity to carbon oxides, hydrogen and water and the conversion of oxygen increases with residence time, it appears that more hydrocarbon oxidation occurs upon longer residence times. Longer residence times are the most convenient conditions for POX in order to avoid formation of hydrocarbon byproducts. However, a more important observation is that the selectivity to hydrogen was hardly influenced by the variation in the total flow rate. These results are also in a good agreement with the work of Witt and Schmidt [16] on the partial oxidation of methane over the Rh coated catalyst. They reported that lower flow rates caused higher production of CO_2 and H_2O. On the other hand, the higher flow rates contributed to enhanced hydrocarbon production.

Table 1
Comparison of blank experiments (unimpregnated Al_2O_3 foams) and experiments over 0.1 wt.% Rh/Al_2O_3 foams for POX and OSR of propane

	POX		OSR	
	Blank experiment	0.01 wt.% Rh/Al_2O_3	Blank experiment	0.01 wt.% Rh/Al_2O_3
Furnace temperature (°C)	800	700	750	700
Maximum reactor temperature (°C)	971	933	892	864
Conversion of C_3H_8	1.00	1.00	0.99	0.96
Conversion of O_2	0.99	1.00	0.94	1.00
Selectivity to H_2	0.37	0.72	0.15	0.92
Selectivity to CO	0.61	0.80	0.45	0.70

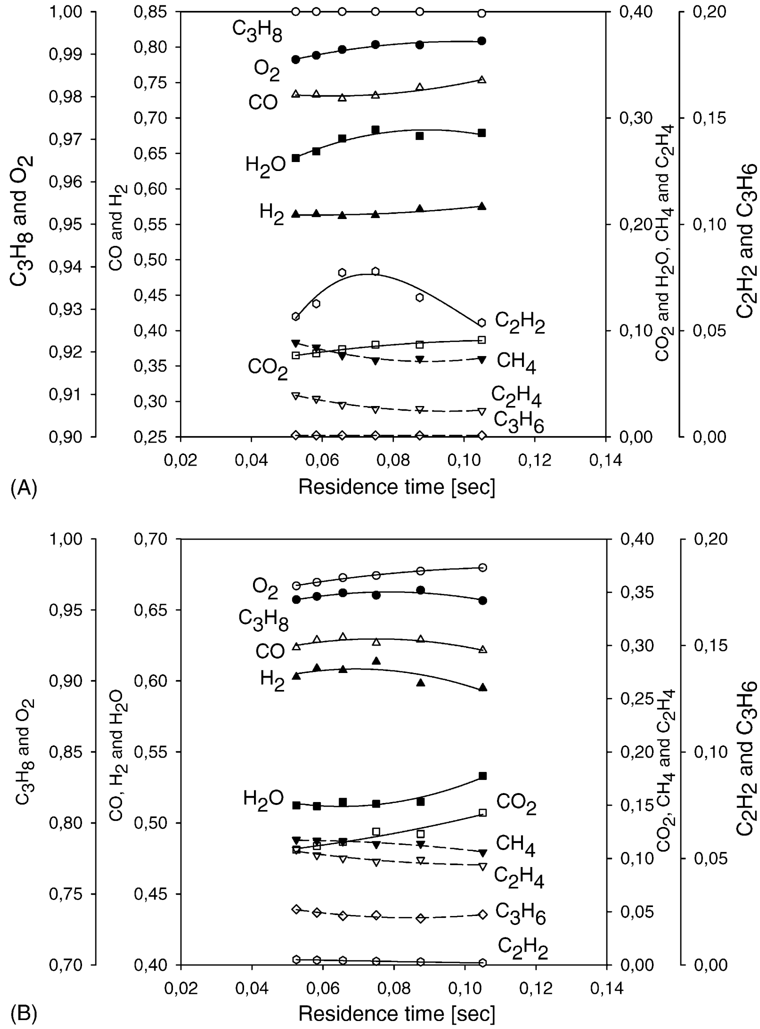

Fig. 5. Effect of the total flow rate for POX (A) and OSR (B) of propane over 0.01wt.% Rh/Al_2O_3 foam. Total flow rates: 1000–2000 N ml/min. Furnace temperature: 700 °C. (A) Feed flows (N ml/min): C_3H_8 (101–203), O_2 (190–380), and N_2 (709–1417). (B) Feed flows (N ml/min): C_3H_8 (100–200), O_2 (150–300), N_2 (450–900), and H_2O (300–600).

In the case of the oxidative steam reforming (Fig. 5B), pronounced differences exist compared to partial oxidation. The selectivity to carbon monoxide and hydrogen seems to have a maximum at approximately 1400 N ml/min. This suggests that products formed via partial oxidation are obtained with the highest yields at this total flow rate. At higher flow rates, more complete oxidation appears to take place as indicated by the increased selectivity to carbon dioxide and water. In addition, the already low ethyne formation gradually decreases with residence time as is also observed for the other hydrocarbons. This implies that maximum formation of ethyne occurs at shorter residence times in this case, and equally for the other hydrocarbons. Total flow rates of 1400 ml/min appear to be optimal for the formation of hydrogen via OSR of propane in this system although the production of hydrocarbons is not minimal. The maximum reactor temperature clearly increases with decreasing residence time for POX as well as for OSR; an observation, which has already been reported for POX of methane [16]. According to the temperature profiles measured along the reactor, the maximum reactor temperature was observed to move towards the outlet with shorter residence time.

These results show that the conversion of oxygen slightly increased with residence time (Fig. 5A and B). However, higher total amounts of oxygen and propane were present in the feed with higher total flow rates. This indicates that overall reaction rates of POX and OSR increase with shorter residence times, since larger amount of reactants (mol/s) were turned over. This observation together with changes in temperature profiles indicate that the reactant flow rate influences mass transfer conditions, which are often rate limiting in such reactor systems.

3.3. Time-on-stream

The conversion of propane and oxygen remained constant over 7 h in the case of partial oxidation (Fig. 6A). A slight

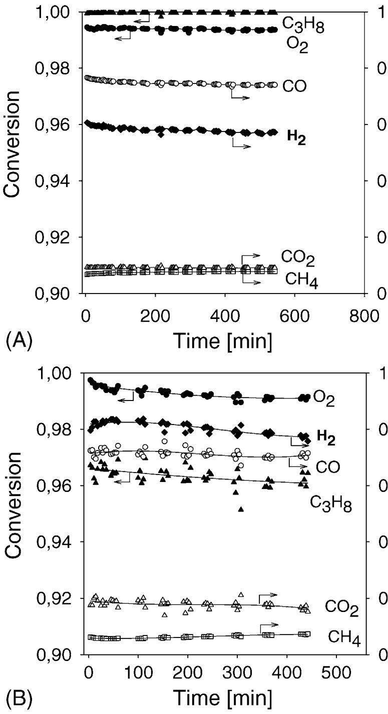

Fig. 6. Conversion of oxygen and propane and selectivity to main products as a function of time-on-stream for partial oxidation of propane (A) and oxidative steam reforming of propane (B) over 0.01wt.% Rh/Al_2O_3 foam. Total flow rate: 1000 N ml/min; furnace temperature: 700 °C. (A) Feed flows (N ml/min): C_3H_8 (101), O_2 (190), and N_2 (709). (B) Feed flows (N ml/min): C_3H_8 (100), O_2 (150), N_2 (450), and H_2O (300).

decrease in the selectivity to hydrogen and carbon oxides and a slight increase in the selectivity to all the detected hydrocarbons were observed. However, these changes in product distribution mainly occurred during the first couple of hours, after which the catalytic activity of the Rh/Al_2O_3 foam catalyst remained stable.

Indications of more pronounced deactivation during the 7-h period were found when steam was present in the reactant mixture (OSR) (Fig. 6B), since the oxygen conversion decreased from 99.7 to 99.1%. The selectivity to hydrogen and carbon oxides was reduced and the selectivity to all hydrocarbon byproducts slightly increased, as was also observed in the case of POX. The Rh foam catalyst may therefore also show an acceptable stability under oxidative steam reforming conditions. A good stability of Rh catalysts under strong oxidation condition has been reported previously [31]. However, further experiments must be performed over the Rh catalyst in terms of days or weeks before any conclusion can be drawn.

3.4. Sensitivity to experimental conditions

Even though the experiments always were performed at close to atmospheric pressure, a needle valve was used to maintain a slightly higher than atmospheric pressure in order to enable gas sampling for product analysis. Interesting and somewhat surprising effects of variations in this overpressure were revealed during POX and OSR over unimpregnated Al_2O_3 foams, where only gas phase reactions occur. At constant furnace temperature and by increasing pressure difference from 0.05 to 0.30 bar, a large impact on the reactions was observed (Fig. 7A). The temperature profiles also revealed that the maximum reactor temperature increased with the pressure difference. The conversion of oxygen and propane increased with the pressure. Increasing the overpressure virtually affected the selectivity to all products. While the selectivity to carbon dioxide and propene decreased with increasing pressure, the selectivity to carbon monoxide, hydrogen, methane, ethane and ethene increased.

However, when the same type of experiment (OSR) was performed over the Rh foam catalyst, main the features of the reaction were almost independent of the pressure difference (Fig. 7B). An effect of the pressure difference can be detected for the conversion of propane, which increased slightly with increasing pressure difference. Otherwise, the selectivity of carbon oxides, hydrogen and water remained almost constant over the pressure range studied. The selectivity to methane, ethane, ethene, ethyne increased with increasing pressure difference whereas the propene selectivity decreased. This is identical to what was observed over the unimpregnated Al_2O_3 foam, and points to the dominant role of gas-phase reactions in the formation of

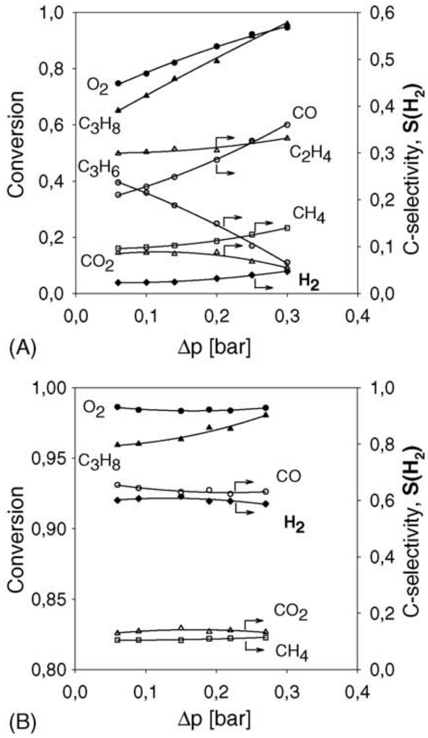

Fig. 7. Effect of the pressure difference (Δp) on OSR of propane over the unimpregnated Al_2O_3 foam (A) and over the 0.01 wt.% Rh/Al_2O_3 foam (B). Total flow rate: 1000 N ml/min; furnace temperature: 700 °C; feed flows (N ml/min): C_3H_8 (100), O_2 (150), N_2 (450), and H_2O (300).

hydrocarbon byproducts under conditions such as those applied here. The maximum reactor temperature changed from 873 to 878 °C, insignificant compared to the changes observed over the unimpregnated Al_2O_3 foam. These results show that not only the reactor/furnace temperature and temperature profiles, but also slight pressure variations in the system are very important for the interpretation of the results. Careful performance of the experiments with respect to pressure control and temperature measurements is thus essential, and particularly when the influence of homogeneous reactions is to be discussed.

4. Conclusion

High selectivity to hydrogen was obtained during both partial oxidation and oxidative steam reforming of propane over Rh-impregnated Al_2O_3 foam catalysts. A furnace temperature of 700 °C was identified as an optimal temperature for hydrogen production by POX as well as by OSR for our system. This temperature was also low enough to maintain a relatively low formation of hydrocarbon byproducts. When comparing partial oxidation and oxidative steam reforming over the 0.01 wt.% Rh/Al_2O_3 foam, the highest yield of hydrogen was obtained by oxidative steam reforming. Experiments where the total flow rate was varied indicate only a minor influence of residence time on the product distribution. The production of hydrogen was hardly affected by the variation of the total flow rate. However, hydrocarbon byproducts are detected in larger amounts at shorter residence time, while higher selectivity to carbon dioxide and water is obtained at longer residence time. Longer residence times apparently allow for hydrocarbon byproducts to be oxidised. Lower total flow rates may thus be required for the minimisation of unwanted products.

Promising stability of the 0.01 wt.% Rh/Al_2O_3 foam catalyst was observed during several hours of operation. A stronger tendency to deactivation was registered when steam was present in the feed (OSR). A systematic study was performed on the variation in the pressure difference usually applied for sampling from the product stream. It was shown that small changes of this overpressure significantly influenced gas-phase reactions and reactor temperatures. Experiments over the 0.01 wt.% Rh/Al_2O_3 foam catalyst, however, revealed only a small effect of the pressure difference on the product distribution; i.e. a minor increase in reactor temperature and propane conversion with increasing pressure.

Acknowledgement

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