

Catalytic conversion of propane to hydrogen in microstructured reactors

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Abstract

A microstructured reactor has been fabricated from the high temperature alloy Fecralloy (72.6% Fe, 22% Cr, 4.8% Al). The reactor was oxidized at high temperature to form a porous layer of α -Al₂O₃ on the surface of the channels and subsequently impregnated with Rh. The reactor was tested for partial oxidation (POX) and oxidative steam reforming (OSR) of propane at 1 bar and in the temperature range 500–1000 °C. The results were compared to those obtained from equivalent experiments using reactors made of pure Rh or from oxidized Fecralloy reactors without catalyst or impregnated with Ni. OSR gives higher yields of hydrogen than POX for the Rh/Al₂O₃/Fecralloy system. Formation of H₂, CO, CO₂ and H₂O by gas phase reactions does not seem to play a dominating role below 1000 °C. Small amounts of methane and ethene were detected at the highest temperatures. The Rh/Al₂O₃/Fecralloy reactor gives higher selectivities to hydrogen as compared to the reactor made of Rh, indicating that having the catalyst dispersed on a porous layer in the microchannels is beneficial. Changing the residence time by changing the feed rate influenced conversions and selectivities differently for Rh/Al₂O₃/Fecralloy and for Al₂O₃/Fecralloy without any Rh. Deactivating including coke formation was not observed for the Rh/Al₂O₃/Fecralloy system under the conditions applied. Results from Ni/Al₂O₃/Fecralloy are more ambiguous, and it appears that sintering effects, oxidation of Ni or possibly loss of material occur in this system. Microstructured Fecralloy foils were prepared in the same way as used for the reactors in order to characterize the resulting oxide layer and the impregnated catalyst. XRD, SEM/EDX and XPS measurements confirm the existence of an α -Al₂O₃ layer. XPS furthermore confirms the presence of metallic Rh, while Ni appears to be present as both metal and oxide. © 2004 Elsevier B.V. All rights reserved.

Keywords: Microstructured reactors; Hydrogen production; Catalytic partial oxidation; Steam reforming; Rh; Ni; Fecralloy; Propane

1. Introduction

The predicted depletion of fossil fuels in the future requires alternative energy systems such as fuel cells using hydrogen as the energy carrier. Today, hydrogen is most efficiently made from natural gas, and fossil fuels will continue to be the primary source for hydrogen for many years, contributing to the development of fuel cells and associated technologies for renewable energy. In the future, hydrogen will have to be produced from biomass or by water electrolysis using renewable energy. Compared to the conventional internal combustion engine, fuel cells are more energy efficient and have lower emissions of pollutants and greenhouse gases.

Norway has 2–3% of the total world production of natural gas [1]. Liquid petroleum gas (LPG) is separated from methane and ethane before methane is piped or shipped to

the market. Norway therefore has a surplus of LPG (mostly propane). Propane is liquid under moderate pressure and is therefore a favorable feedstock for distributed hydrogen production since it is easy to store and transport. A distribution net is also partially developed.

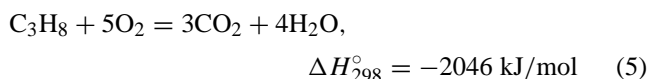
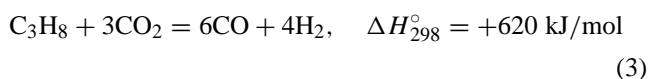
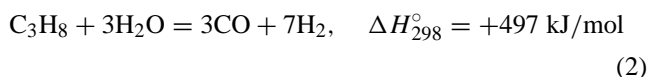
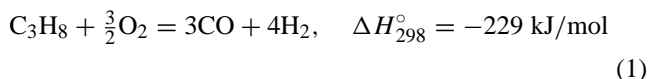
Microstructured reactors are small and compact and thus interesting for small-scale applications for distributed or mobile hydrogen production. The large surface-to-volume ratios in these reactors lead to good heat and mass transfer properties and hence process intensification. Since the small channel dimensions (20–1000 μ m) often lie below the quenching distance, explosive gas mixtures can be handled safely [2]. Metallic reactors facilitate high thermal conductivity, which is essential when combining exothermic and endothermic reactions to ensure a good axial heat transport and avoid hot-spots [3]. The reactors can be made from the catalytic metal itself or impregnated with the catalytic material after fabrication. The use of small amounts of catalytic material dispersed on a porous surface inside the microchannels is in many cases desirable, but more elaborate to achieve [4].

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Hydrogen can be produced from propane through partial oxidation (1) and steam (2), or dry reforming (3). Oxidative steam reforming (OSR) is a combination of partial oxidation and steam reforming, where the oxidation provides heat for the endothermic reforming reactions. Water–gas shift (WGS) (4) and total oxidation (5) will normally play a role, depending on reactant composition, temperature and heat transfer rate, residence time and the catalytic system involved.



Two different mechanisms for the catalytic partial oxidation have been proposed in the literature. The first follows a scheme involving catalytic combustion (5), where all the oxygen is consumed, followed by endothermic steam (2) and CO_2 reforming (3) as well as water–gas shift (4) [5–8]. Given sufficient residence time, the product gas composition is determined by thermodynamic equilibrium at the exit temperature of the reaction zone. Since water–gas shift and reforming are relatively slow reactions compared to oxidation reactions, these reactions may not strongly affect the product distribution at very short contact times [9,10]. In such a case, composition of the product gas will not be determined by equilibrium. The other proposed mechanism suggests that H_2 and CO form as direct products from catalytic partial oxidation (1). This has been confirmed experimentally to be the case for very short contact times [11–16]. The yield of synthesis gas through this direct route is, however, limited because the products are more reactive towards combustion than the reactant [17].

Addition of steam to reactant mixtures containing propane and air should in principle lead to higher hydrogen yields as a consequence of the effect of water on the equilibria for reactions (2), (3) and (4), provided that the heat from the oxidation can be readily transferred to the reforming zone of the catalytic system.

Strong gradients in temperature and volumetric flow will be present in such a reaction system. It has been proposed that high linear gas velocities will increase the mass transfer in the reactor by reducing the film/boundary layer thickness, thereby increasing the reaction rates. Partial oxidation over

Pt gauze catalyst [17] has clearly showed this behavior. In microchannel reactors, however, the small channel dimensions should lead to a lower influence of the boundary layer mass transfer limitation [18].

Temperatures in the range 600–1000 °C or higher, are required to obtain high yields of hydrogen and carbon monoxide. As the temperature approaches 1000 °C, the reactions can no longer be viewed as purely catalytic, since gas phase reactions will play an increasingly important role. Reactions leading to the formation of side-products as well as solid carbon (coke) must also be considered. The latter is particularly unwanted and generally occurs when the C/O ratio in the reactant mixture becomes too high. The extent of carbon formation is also related to the type of hydrocarbon feed (alkanes/olefins) involved and the amount of steam and/or oxygen added to the feed.

The best choice of catalyst to produce hydrogen-rich synthesis gas by catalytic partial oxidation of lower alkanes is Rh [19,20]. Ni-based catalysts are by far the preferred systems for steam reforming, due to activity as well as cost considerations. It is thus probably the preferred catalyst for oxidative steam reforming [21]. However, Ni is not the best oxidation catalyst, since it is more easily oxidized and prone to sintering and loss upon exposure to very high temperatures [9]. A combination of the properties of noble metal oxidation catalysts and Ni would probably be ideal, but not readily realized in combination with efficient heat transfer.

The scope of this work was to study small-scale hydrogen production by partial oxidation and oxidative steam reforming of propane in microstructured reactors. Investigations of propane conversion and hydrogen yield as a function of catalyst material and structure, residence time and feed gas composition have been performed.

2. Experimental

The reactors were manufactured at the Institute for Micro Process Engineering (IMVT) at Forschungszentrum Karlsruhe from rhodium or Fecralloy (72.6% Fe, 22% Cr, 4.8% Al) foils with micromachined channels of approximately 120 μm \times 130 μm or 100 μm \times 120 μm cross section. The microstructured foils were stacked and electron beam welded into compact honeycomb reactors [22].

Physical data for the reactors are given in Table 1. The Fecralloy reactors (reactors 2–4) were all oxidized in air at 1000 °C for 4 h to form a thin, porous $\alpha\text{-Al}_2\text{O}_3$ surface layer, and subsequently impregnated with the catalytic metal. After oxidation the specific surface area of reactor 4 was measured by Kr-BET (Quantachrome Autosorb 1c). Reactor 2 was impregnated with Rh by passing an aqueous solution of RhCl_3 through the channels several times, followed by drying at 120 °C overnight and reduction at 800 °C for 3 h in 10% hydrogen in nitrogen. Similarly, reactor 3 was impregnated with Ni using a saturated aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, followed by drying at 120 °C

Table 1
Physical data of the microstructured reactors

Reactor no.	1	2	3	4
Material	Rhodium	Fecralloy	Fecralloy	Fecralloy
H × W × L (mm ³)	5.5 × 5.6 × 20	5.5 × 5.6 × 20	5.5 × 5.6 × 20	5.5 × 5.6 × 20
Channels	676	676	676	676
Channel dimension (μm ²)	120 × 130	120 × 130	120 × 130	100 × 120
Geometric surface of channels (cm ²)	67.5	67.5	67.5	59.5
Porosity	0.34	0.34	0.34	0.26
Residence time, τ (ms) at 1 NI/min	12.6	12.6	12.6	9.7
Impregnated with	–	Rh	Ni	–

overnight, calcination at 600 °C for 4 h in flowing air and reduction in 10% hydrogen at 600 °C for 1 h. The mass increase resulting from impregnation corresponds to 1 mg Rh and 30 mg Ni deposited in the channels of each reactor, respectively. The oxidized and impregnated Fecralloy reactors will hereafter be referred to as either Rh/Al₂O₃/Fecralloy or Ni/Al₂O₃/Fecralloy, whereas the reactor made from Rh foils is simply called the Rh reactor.

In order to further investigate the structure and chemistry of the resulting porous catalytic layer in the microchannel walls of the reactors, single microstructured Fecralloy foils were subjected to the same oxidation and impregnation procedure as described above for the reactors. Oxidized foils were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX) and X-ray diffraction (XRD). Oxidized, impregnated and reduced foils were subjected to X-ray photoelectron spectroscopy (XPS) investigation. Preparation was conducted ex situ, and the foils were thus exposed to air between preparation and loading into the XPS vacuum system.

Reaction studies were performed both at IMVT, Karlsruhe and SINTEF/NTNU, Trondheim using different reactor housings. In the experimental set-up at IMVT the reactor housing, described in detail elsewhere [18], contained a ceramic holding unit for the microstructured reactor equipped with a heating wire for rapid heating. At SINTEF/NTNU the microstructured reactor was placed in a quartz tube placed in a transparent, gold-insulated furnace (Thermcraft Trans Temp). The product gas temperature was measured with a thermocouple at the reactor exit in both set-ups. In addition, the catalyst temperature at the exit of the reactor was monitored by a pyrometer through a quartz window in the IMVT set-up. The difference in these two measurements was always within 5%. The product gas mixtures were analyzed by gas chromatography (Agilent 6890 at IMVT and Agilent G2891A MicroGC at NTNU/SINTEF).

A mixture of propane and synthetic air was used in the partial oxidation experiments. Preliminary experiments indicated that the optimum C/O-ratio was around 0.80–0.85, in accordance with literature values [23]. During OSR experiments, the propane concentration was kept the same as for POX, and the H₂O/O₂-ratio was 2. The C/O-ratio (including O₂ and H₂O oxygen) was lowered to 0.5 to avoid

Table 2
Feed gas composition (vol.%) for partial oxidation (POX) and oxidative steam reforming (OSR)

Feed gas component	POX	OSR
Propane	10.2	10.2
Oxygen	19.0	15.3
Water	–	30.6
Nitrogen	70.8	43.9

coke formation. For complete feed gas compositions, see Table 2. Nitrogen was used as an internal standard in the GC-analysis. All experiments were conducted at 1 bar with a pressure drop within 5% of the total pressure. The residence time was changed by changing the total flow, holding the feed gas composition constant.

In order to compare different experiments, the hydrogen selectivity $S(\text{H}_2)$ was calculated as follows:

$$S(\text{H}_2) = \frac{Q_{\text{tot,out}}}{Q_{\text{tot,in}}} \frac{C_{\text{H}_2,\text{out}}}{4C_{\text{C}_3\text{H}_8,\text{in}} X_{\text{C}_3\text{H}_8}} \quad (6)$$

$Q_{\text{tot,in}}$ is total volumetric gas flow at reactor inlet and $Q_{\text{tot,out}}$ is the total volumetric gas flow at reactor exit in NI/min at STP (0 °C, 101.3 kPa). $C_{\text{H}_2,\text{out}}$ is the hydrogen concentration in the product gas, $C_{\text{C}_3\text{H}_8,\text{in}}$ is the propane concentration in the feed gas and $X_{\text{C}_3\text{H}_8}$ is the conversion of propane. This selectivity quantifies how much hydrogen that is obtained relative to the amount of propane converted, irrespective of whether steam was added to the reactant mixture or not. It may thus exceed 1 for OSR experiments.

The residence times given are based on gas hourly space velocity (GHSV) of the feed gas at STP, and are calculated as follows:

$$\tau = \frac{V_{\text{channels}}}{Q_{\text{tot,in}}} \quad (7)$$

V_{channels} is the total volume of the microchannels in the reactor.

3. Results and discussion

The total surface area of reactor 4 after oxidation was measured by Kr-BET to be 680 cm², around 10 times higher

than the total geometric surface area, which was estimated to 65 cm². The surface area before oxidation was too small to be measured by adsorption.

XRD analysis confirm that aluminum oxide in the form of α -Al₂O₃ is the dominant crystalline phase formed on the Fecralloy surface upon high temperature oxidation, which was to be expected from previous work [24]. The XPS results for Al2p and O1s also fit well with Al₂O₃, but the presence of some metallic Al can not be completely ruled out. Traces of Fe and Cr are detected to very small levels (1–2% or lower) and exist probably in oxidic form if present on the surface. Considering that photoelectrons probe at most 10–20 nm (usually less) into the sample, it can be concluded that the alumina film covers the surface well. SEM/EDX analysis of the foil cross section reveals the presence of an aluminum oxide layer less than 10 μ m thick, but varying in thickness.

The XPS experiments furthermore show Rh 3d peaks that correspond relatively well with metallic Rh for the Rh-impregnated foils, but indications of small amounts of chemically bound Rh are found. The amount of Rh in the surface estimated from a qualitative analysis of the data is around 3%. XPS results on the Ni-impregnated foils indicate that Ni is present both as metallic Ni and in at least one chemically bound state, most likely Ni₂O₃, from analysis of Ni2p and 3p peaks. The quantification appears to underestimate the amount of Ni in the surface, about 3–6%, since quite high loading of Ni was predicted by weighing the reactor after impregnation. The analysis will in such cases be ambiguous due to its dependence of the structure of Ni, i.e. particle shape and size, as well as impurities introduced by exposing the samples to air between reduction and XPS analysis. The XPS analyses show few impurities except those resulting from exposure to air. Possible traces of the impregnation salts, i.e. nitrogen and chlorine, are below the detection limit.

Product gas composition as a function of the measured product gas temperature for POX in the Rh/Al₂O₃/Fecralloy reactor is given in Fig. 1. The feed rate of 1 Nl/min gives a residence time of 12.6 ms. It can be observed that total oxidation to water and CO₂ is dominant below 600 °C. An increase in the temperature favors endothermic reforming reactions, leading to higher hydrogen production. Complete conversion of propane is obtained at 1000 °C. At this temperature, hydrogen and CO concentrations of ~17 and ~15% are obtained, corresponding to selectivities of ~58 and ~66%, respectively.

Fig. 2 shows the product gas composition for OSR in the same reactor with the same feed rate of propane as in Fig. 1. Similar to POX, total combustion is more dominant at temperatures lower than 600 °C, and complete conversion is obtained at 1000 °C. The corresponding hydrogen and CO concentrations are in this case ~25 and ~13%, equivalent to selectivities of ~87 and ~60%, respectively. Addition of steam increases hydrogen and decreases CO formation relative to partial oxidation using the same concentration of propane. The total amount of syngas (H₂ + CO) increases

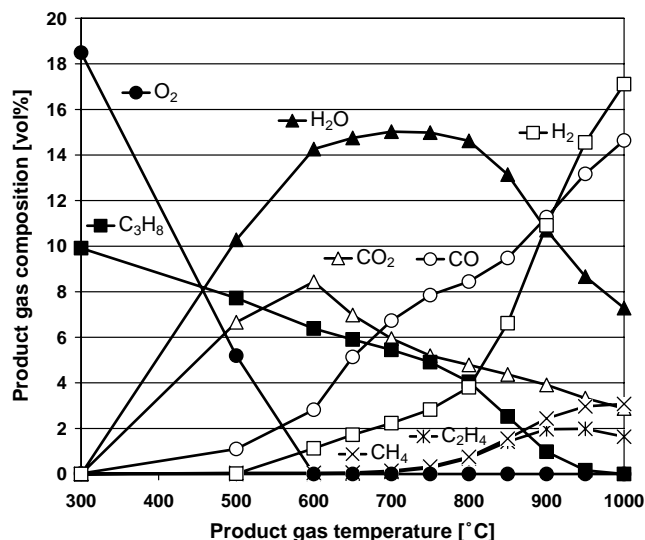


Fig. 1. Product gas composition as a function of the measured gas temperature for partial oxidation of propane in a Rh/Al₂O₃/Fecralloy reactor ($\tau = 12.6$ ms).

by almost 30%. This confirms that not only WGS but also reforming takes place to a higher extent for OSR.

Experiments using an oxidized Fecralloy reactor without any catalyst were performed in order to possibly distinguish catalytic effects from contributions of gas phase reactions. Fig. 3 compares the results of catalytic partial oxidation at varying residence times in the Rh/Al₂O₃/Fecralloy and oxidized Fecralloy reactors. Propane as well as oxygen conversion is substantially higher at all residence times and temperatures when Rh is present. Oxygen conversion is complete at all temperatures shown for the catalytic reaction. The lack of points at lower temperatures for the

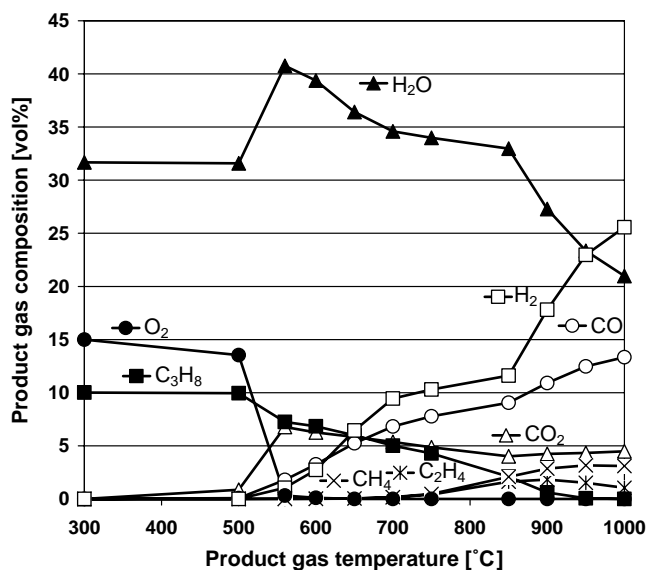


Fig. 2. Product gas composition as a function of the measured gas temperature for oxidative steam reforming of propane in a Rh/Al₂O₃/Fecralloy reactor ($\tau = 12.6$ ms).

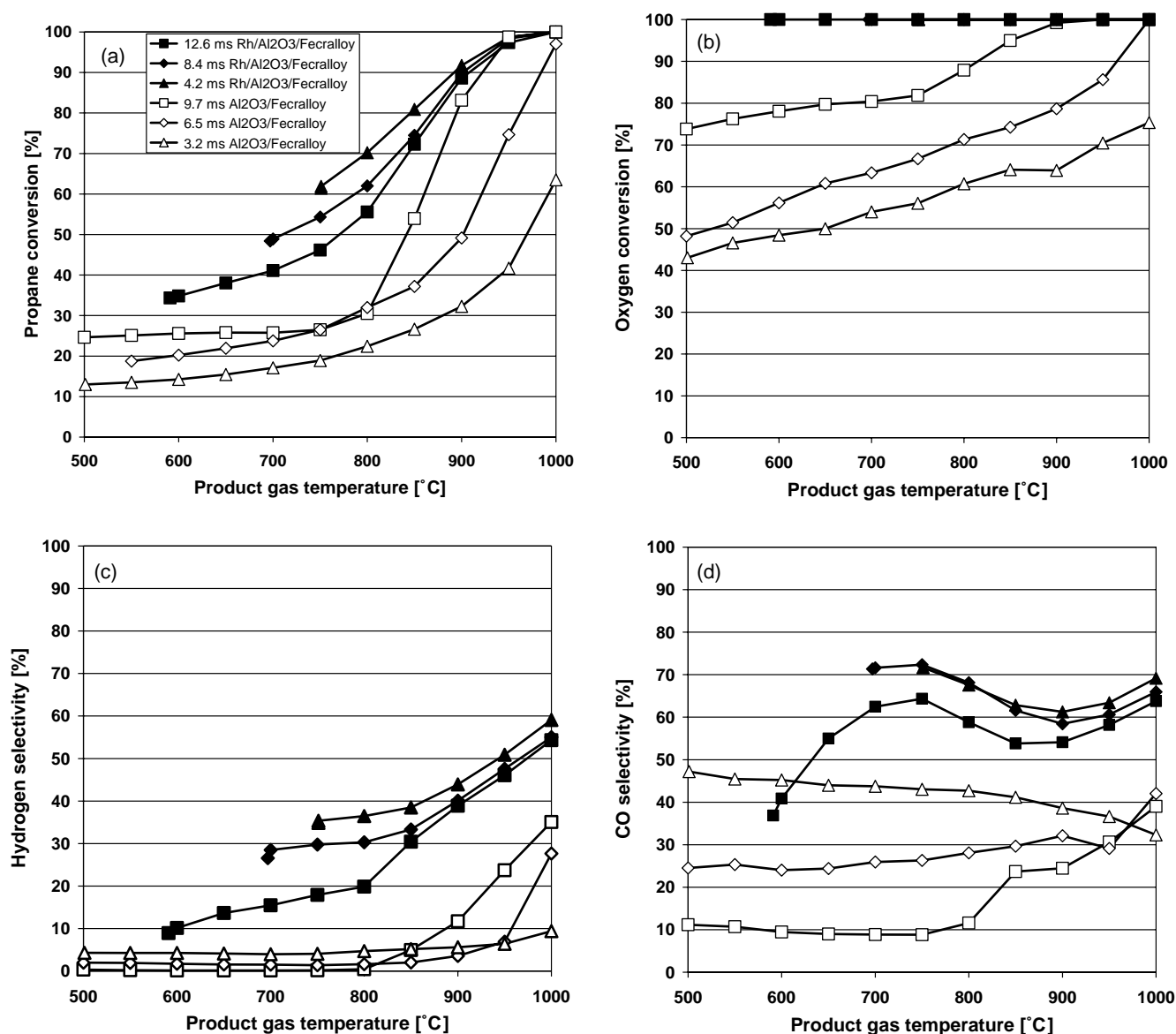


Fig. 3. Partial oxidation of propane in the Rh/Al₂O₃/Fecralloy (filled symbols) reactor and an oxidized Fecralloy reactor without any catalyst (open symbols) at different residence times as a function of the measured gas temperature. (a) Propane conversion; (b) oxygen conversion. Total oxygen conversion was obtained for all residence times in the Rh/Al₂O₃/Fecralloy reactor. (c) Hydrogen selectivity; (d) CO selectivity.

catalytic reaction originates from the ignition-extinction behavior of the reaction: At the lowest temperatures displayed, the reaction is self-sustained and lower temperatures can not be obtained by changing the furnace temperature. Propane conversion is complete above 950–1000 °C when Rh is present, whereas this is the case only for the longest residence times when no catalyst is present.

The selectivities to hydrogen and CO also benefit from the catalyst. They are in the range 54–60% (H₂) and 64–70% (CO) with catalyst, as compared to 8–35% (H₂) and 32–42% (CO) without using any catalyst at the highest conversions and temperatures. Fig. 3 furthermore demonstrates that the contribution from gas phase reactions is increasing with increasing temperature, as to be expected. By increasing the

temperature further beyond 1000 °C, gas phase reactions should play a gradually more dominant role compared to the catalytic reactions. When steam is added as a reactant (OSR experiments not shown here) the trends are the same with respect to the catalytic effect of Rh on Fecralloy in the temperature range 500–1000 °C. Also in this case, the contributions from gas phase reactions increase rapidly as the temperature approaches 1000 °C.

As observed in Figs. 1 and 2, some methane and ethene are found in the product gas for both POX and OSR, at approximately the same levels. Comparable amounts are observed in equivalent experiments over the oxidized Fecralloy reactor with no catalyst, indicating that the side-products are mainly formed through thermal cracking. No changes

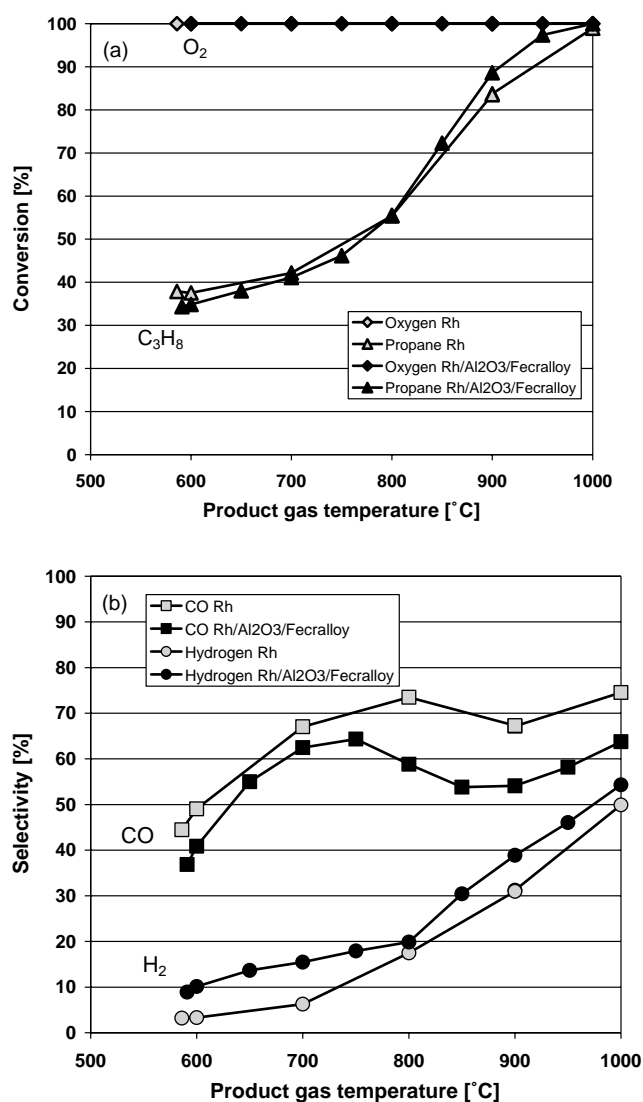


Fig. 4. Comparison of the Rh/Al₂O₃/Fecralloy reactor (black symbols) with a Rh reactor (gray symbols) for partial oxidation of propane as a function of the measured gas temperature. (a) Propane and oxygen conversions; (b) hydrogen and CO selectivities ($\tau = 12.6$ ms).

in pressure drop or other indications of coke formation were observed in any of the experiments reported here. The Rh/Al₂O₃/Fecralloy reactors show no signs of deactivation upon repeated cycling. However, systematic deactivation studies remain to be performed along with studies of Rh particle size, dispersion and structure, and changes in these properties with time-on-stream.

The POX experiments show that the Rh/Al₂O₃/Fecralloy reactor gives a higher hydrogen yield (58%) than the Rh reactor (50%) but a lower CO yield (66% as opposed to 75%) for complete conversion of propane, as shown in Fig. 4. The propane conversion is not strongly affected, and the conversion of oxygen is complete for both systems. This indicates that having the catalyst dispersed as small particles on the surface does not affect the activity of oxidation and

reforming reactions (1–3) to any great extent, but seems to be beneficial for the WGS activity (4).

OSR experiments with freshly impregnated Ni/Al₂O₃/Fecralloy seem to give lower conversions as well as lower selectivities towards H₂ and CO than with the Rh/Al₂O₃/Fecralloy reactor. Also, the activity of the Ni/Al₂O₃/Fecralloy system decreases relatively fast during the first couple of cycles, indicating possible sintering of the Ni-particles, coking, oxidation of Ni or loss of catalytic material by formation of volatile Ni-species. Alternative methods for impregnating the Fecralloy reactor with Ni particles could be considered.

When reducing the residence time, conversions and selectivities are affected differently dependent on whether catalyst is present or not (Fig. 3). The residence time is decreased by increasing the total flow. Since the conversion of oxygen is complete for all residence times, the rate of heat generation by catalytic combustion will increase. This may result in increasing surface temperatures in the Rh/Al₂O₃/Fecralloy system. This heat will supply the endothermic reforming reactions to a greater extent, which could explain the residence time effects observed for the catalytic system in Fig. 3. The same temperature increase will not take place in the Al₂O₃/Fecralloy system and an increase of the residence time in this system results in less contributions from reforming reactions, hence the opposite residence time effect for this system.

4. Conclusions

Oxidative steam reforming of propane results in increased yield of hydrogen compared to catalytic partial oxidation (POX) over a Rh/Al₂O₃/Fecralloy microstructured reactor system. POX and OSR experiments using an oxidized Fecralloy reactor with no catalyst show that formation of H₂, CO, CO₂ and H₂O by gas phase reactions does not seem to play a dominating role below 1000 °C. Small amounts of methane and ethene are detected at the highest temperatures. The Rh/Al₂O₃/Fecralloy reactor gives higher yield of hydrogen as compared to a microstructured reactor made from pure rhodium, indicating that having the catalyst dispersed on a porous layer in the microchannels is beneficial. Changing the residence time by changing the feed rate influenced conversions and selectivities differently for Rh/Al₂O₃/Fecralloy and for Al₂O₃/Fecralloy without any Rh. Neither coke formation nor any other form of deactivation of the Rh/Al₂O₃/Fecralloy system was observed under the conditions applied. Results on Ni/Al₂O₃/Fecralloy are more ambiguous, and it appears that sintering effects, oxidation of Ni or possibly loss of material occur in this system. Microstructured Fecralloy foils were prepared in the same way as the reactors in order to characterize the resulting oxide layer and impregnated catalyst. XRD, SEM/EDX and XPS measurements confirm the existence of an α -Al₂O₃ layer. XPS furthermore confirms presence of metallic Rh,

while Ni appear to be present in both metallic and chemically bound states.

Acknowledgements

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