THE CATALYTIC INFLUENCE OF THE REACTOR MATERIAL ON THE REFORMING OF METHANOL IN SUPERCRITICAL WATER

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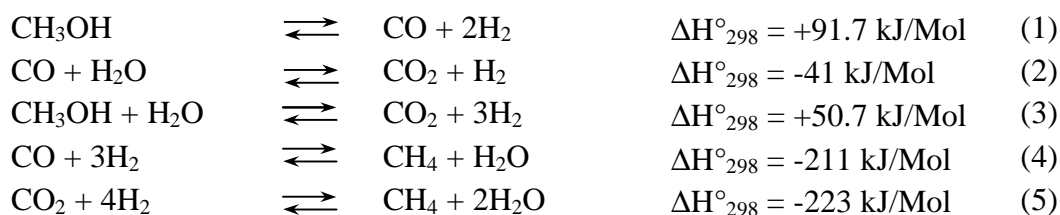e-mail: Volker.Diem@itc-cpv.fzk.de

The reforming of methanol in supercritical water was studied in continuously operated tubular reactors made of the nickel base alloy INCONEL 625 and stainless steel SS 316. Experiments were performed at 25 MPa and 600° C. The flow rate of the feed solution ranged from 6 to 300 ml/h. The main component of the product gas was hydrogen with smaller amounts of carbon dioxide, carbon monoxide and methane. Methanol conversion was up to 99.9 % without addition of a catalyst. The reforming reaction is catalysed by the heavy metals at the inner reactor surface. Surface materials tested were INCONEL 625, stainless steel SS316, pure nickel and alumina ceramics. Oxidation of the inner surface of the reactor made of INCONEL 625 at supercritical water conditions before the methanol reforming accelerated the reaction rate and reduced the carbon monoxide concentration.

INTRODUCTION

The first study of the methanol reforming reaction dates 1921. The Danish scientist J. A. Christiansen found that a mixture of methanol and water vapor was decomposed at 250°C using copper metal as catalyst [1]. CuO – ZnO catalyst systems turned out to be very active for the methanol steam reforming. These catalysts are rapidly deactivated by impurities such as hydrogen sulfide and chlorine compounds and at higher temperatures. Higher alcohols, which can be found as impurities in commercial methanol, might also reduce the activity of the catalyst.

The overall reaction can be described by five reactions, only three being independent: (1) the methanol decomposition, (2) the water gas shift reaction, (3) the methanol steam reforming, (4) the methanation of carbon monoxide and (5) carbon dioxide. The reforming reaction (3) is endothermic and thus favored at higher temperatures.

Gasification of organic material in supercritical water was first investigated in the ´70s in the USA [2,3]. Even more work on the process of the oxidation of hazardous waste with oxygen or air in supercritical water was published [4]. To study reaction kinetics and reaction mechanisms, the oxidation of the model compound methanol with airborne oxygen in supercritical water has been extensively studied. The results of first screening experiments on methanol reforming in supercritical water have been published by [5] and [6].

CH$_3$OH	$\rightleftharpoons$	CO + 2H$_2$	$\Delta H°_{298}$ = +91.7 kJ/Mol	(1)
CO + H$_2$O	$\rightleftharpoons$	CO$_2$ + H$_2$	$\Delta H°_{298}$ = -41 kJ/Mol	(2)
CH$_3$OH + H$_2$O	$\rightleftharpoons$	CO$_2$ + 3H$_2$	$\Delta H°_{298}$ = +50.7 kJ/Mol	(3)
CO + 3H$_2$	$\rightleftharpoons$	CH$_4$ + H$_2$O	$\Delta H°_{298}$ = -211 kJ/Mol	(4)
CO$_2$ + 4H$_2$	$\rightleftharpoons$	CH$_4$ + 2H$_2$O	$\Delta H°_{298}$ = -223 kJ/Mol	(5)

There are major advantages if the reaction is carried out in supercritical water: the density of supercritical water at 600° C and 250 bar is about one order of magnitude higher than the density of water vapor at 250° C and 5 bar. This leads to a much higher space-time yield. Increased thermal conductivity and higher temperature will promote the endothermic reforming reaction. The required compression work is low due to the low compressibility of the liquid fuel. The gas product on the other side is compressed to about 25 MPa, which is optimum for short time storage.

EXPERIMENTAL

The experiments were performed with reactors made of Inconel alloy 625 or stainless steel SS316. The tubing and the fittings were made of stainless steel SS316. The reactor was a pressure tube of 1000 mm length, an outer diameter of 14.3 mm and an inner diameter of 8.3 mm (see also [6] and [7]). To achieve the required short residence times, the volume of the reactor has been reduced by a cylindrical displacer made of stainless steel SS316 (d=8.0 mm, l=1000 mm) resulting in an annular gap shaped reaction space. Another reactor tube was equipped with a liner and displacers made of pure nickel. A movable thermocouple placed inside a capillary tube (1/16 inch diameter) passed through a centric bore of this cylindrical displacer records the internal temperature profile of the reactor. The temperature gradient between center of the displacer and fluid phase is assumed to be negligible. Three separately regulated electrical heating coils have been used in order to smoothen the temperature profile. The temperature in the reaction zone was 600 ± 10 °C. The ends of the tubes were cooled down to room temperature.

The annular gap measured about 150 μm. This small dimension is characteristic for a micro-reactor-system. Therefor this reactor concept will benefit from the advantages of the micro-reactor-design, mainly enhanced heat transfer and mass transfer. The surface/volume ratio is about 130 cm^{-1}.

In some experiments all of the walls which were in contact with the reacting fluid consisted of alumina. A tube made of alumina ceramics was placed inside an Inconel alloy 625 tube. Displacers made of alumina were used only in the outer parts of the reactor, resulting in a reaction space of 15 cm³.

A HPLC - pump compressed the methanol in water solution with a flow rate from 6 up to 300 g/h. The residence time values were calculated from the flow rate, the density of pure water under reaction conditions and the free inner volume of the reactor. The physical properties of the mixture will change during reaction. This change will be largest for solutions with high methanol concentrations and high conversion. Methanol in the aqueous solution will decompose, the gases H$_2$, CO, CO$_2$ and CH$_4$ will be formed. Because the p,V,T data for the 6-

component system are not available, the exact residence time cannot be computed. The residence time calculated for pure water is used instead as best approach.

After reaction, the product mixture is expanded to atmospheric pressure by a backpressure regulator and the liquid and the gaseous phase are separated in a simple phase separator.

RESULTS AND DISCUSSION

Before the first experiment, the reactor made of alloy 625 was unintentionally used for oxidation work in supercritical water. By this operation the reactor has been pre-oxidized by a treatment with a solution of H_2O_2 in water (3 wt-%) at 600° C and 25 MPa for about 50 hours. Later this treatment turned out to be crucial for high conversion rates and high hydrogen yields. The conversion with a new reactor, which was not pretreated with aqueous H_2O_2-solution, was lower than with the reactor used for the first experiments. After pretreatment of the same reactor with a solution of H_2O_2 in water (3 wt-%) at 600° C and 25 MPa for about 50 hours the conversion increased significantly (more details in [7]).

The analysis of the heavy metal concentration in the aqueous effluent during the H_2O_2 pretreatment showed that chromium and molybdenum are oxidized and preferably dissolved from the inner surface of the reactor. The speciation of chromium in the aqueous effluent showed only Cr(VI).

Analysis of the catalytically active surface was done with the SEM/EDX method. A microphotography of the inner reactor surface after gasification reaction with the BSE detector (this detector shows contrasts in the chemical composition) showed that the surface was covered by small (most of them smaller than 1 µm) grains. The measurement with the EDX method showed that these grains consisted of nickel (about 93 wt%). Obviously the nickel-oxides formed after treatment with H_2O_2 have been reduced during the gasification reaction to pure nickel.

In order to separate the catalytic effect of the INCONEL 625 from that of SS316 (the material of the cylindrical displacers), some of the experiments were done in a reactor made of stainless steel SS316 with displacers made of SS316. This reactor was pretreated with aqueous H_2O_2 solution under the same conditions, but for a longer time (about 130 h). Only low quantities of heavy metals were dissolved. Only molybdenum and chromium could be detected in the aqueous effluent.
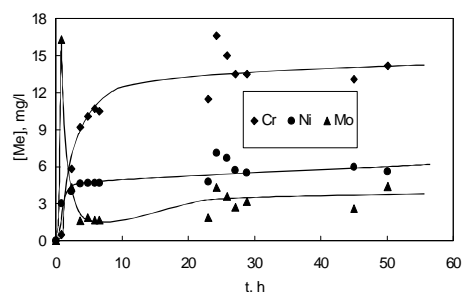

Figure 1: Heavy metal concentration in the aqueous effluent during the H_2O_2 pretreatment (3 wt-%) of the reactor made of INCONEL 625. Experimental conditions: 25 MPa, 600° C, flow rate 0,8 ml/min.

The inner surface of the reactor made of SS316 after performing the methanol reforming experiments was analysed with the SEM/EDX method. The surface was homogeneously covered with iron oxides.
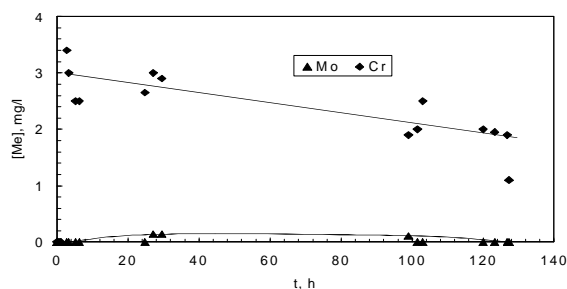
Figure 2: Heavy metal concentration in the aqueous effluent during the H_2O_2 pretreatment (3 wt-%) of the reactor made of SS316. Experimental conditions: 25 MPa, 600° C, flow rate 0,8 ml/min.

The conversion products of methanol in/with supercritical water in all cases were hydrogen, carbon dioxide, carbon monoxide and methane.

The net effect of the variation of residence time on the gas composition and the conversion of methanol at 600° C using an aqueous feed concentration of 50 wt-% methanol is illustrated in figure 3. The gasification of methanol at residence times higher than 8 s was more than 99 %. The hydrogen partial pressure slightly decreased with increasing residence time due to the enhanced methanation reaction. Carbon monoxide and carbon dioxide showed the behavior determined by the water gas shift reaction.

The yield of hydrogen (mol H_2 / mol CH_3OH) is of technical interest. The theoretical gas efficiency of hydrogen according to equation (3) will be 3. The maximum gas efficiency observed was 2.2 for the 50 wt-% methanol solution. At higher residence times, the hydrogen yield decreases steadily. This is due to the consumption of hydrogen by formation of methane (see equations (4) and (5)). The drop of the hydrogen yield at low residence times is caused by the reduced conversion of methanol and the lower percentage of hydrogen formed by the water gas shift reaction (2). Experiments with variied methanol concentrations showed that the reduction of the methanol concentration will raise the hydrogen yield. The higher water surplus favors the water gas shift reaction.
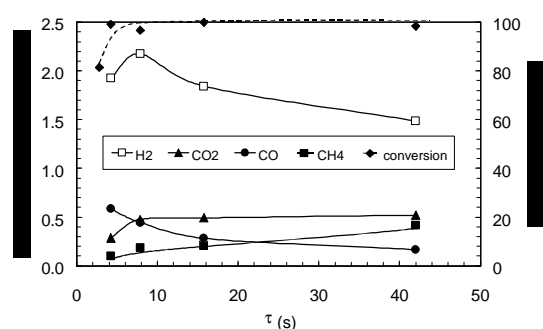

Figure 3: Gas efficiency and methanol conversion as a function of residence time. Experimental conditions: T=600° C, p=25 MPa, aqueous methanol concentration 50 wt-%, reactor material INCONEL 625 with displacers made of SS316.

Changing the reactor material to stainless steel SS316 will result in a much lower conversion of methanol (see figure 4). The maximum residence time measured was about 10 s. The carbon dioxide and hydrogen concentrations in the product gas are similar to the results using INCONEL alloy 625. The CO concentration is significantly reduced (between 2 and 5 vol-%). Due to the lower conversion, gas efficiency is reduced compared to the experiments with a reactor made of INCONEL alloy 625.
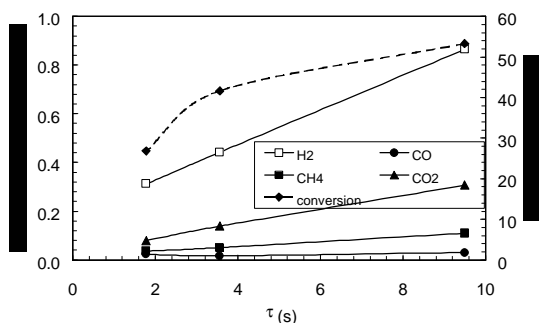
Figure 4: Gas efficiency and methanol conversion as a function of residence time. Experimental conditions: T=600° C, p=25 MPa, aqueous methanol concentration 26.2 wt-%, reactor material SS316 with displacers made of SS316.

Obviously nickel catalyses the methanol decomposition very well. A new reactor made of INCONEL 625 equipped with a lining and displacers made of pure nickel was built; the complete surface in the reaction zone which is in contact with the methanol solution consisted of pure nickel.

Reaction parameters are the same as in the previously shown experiments (figures 3 and 4). At 600° C the conversion of methanol is almost complete. The CO content is lower compared to the reactor with the pre-treated INCONEL 625 inner surface. But there is a strong decrease of the hydrogen content in the product gas with increasing residence time. This is due to the enhanced methanation reaction (equations (4) and (5)). Nickel is a well known methanation catalyst.
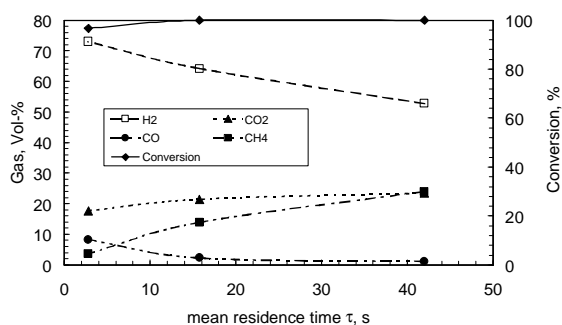

Figure 5: Gas composition and methanol conversion as a function of residence time. Experimental conditions: T=600° C, p=25 MPa, aqueous methanol concentration 26.2 wt-%, the reactor inner surface was made of pure nickel.
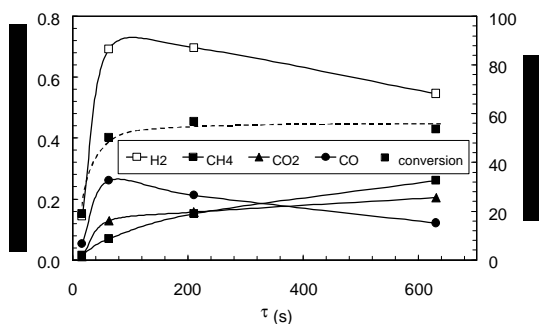

Figure 6: Gas efficiency and methanol conversion as a function of residence time. Experimental conditions: T=600° C, p=25 MPa, aqueous methanol concentration 50 wt-%, reactor material INCONEL 625 with an inner tube and displacers made of alumina ceramics.

Another reactor with the complete surface in the reaction zone made of alumina ceramics was used for another set of experiments. No heavy metals were present which could catalyse the methanol gasification. The results of this non-catalised methanol reforming in supercritical water are shown in figure 6. The maximum conversion observed for residence times higher than 60 s was about 50 %. CO and hydrogen yield decrease with increasing residence time due to the formation of methane. At low residence times conversion and thus gas efficiency was much lower than for the other reactor wall materials tested.

CONCLUSIONS

The methanol conversion in supercritical water is almost complete if reactors with an inner surface made of pure nickel is used. Reactors made of INCONEL 625 with pre-treated inner surface (oxidation with 3 wt-% aqueous H_2O_2-solution) show comparable high performance with respect to the methanol conversion. This reactors will lead to the highest hydrogen yield (mol H_2 / mol CH_3OH). The hydrogen yield is reduced if reactors with an inner surface consisting of pure nickel are used because of the higher methane yield. Reactors made of stainless steel SS316 show poor performance, the methanol conversion and as a consequence the hydrogen yield are low.

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