DEVELOPMENT OF MICRO-STRUCTURED CATALYTIC WALL REACTORS FOR HYDROGEN PRODUCTION BY METHANOL STEAM REFORMING OVER NOVEL Pt/In$_2$O$_3$/Al$_2$O$_3$ CATALYSTS

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Methanol steam reforming was investigated over novel Pd/In$_2$O$_3$/Al$_2$O$_3$ and Pt/In$_2$O$_3$/Al$_2$O$_3$ catalysts coated into microchannels. The investigations revealed, that Pt is much more active at still moderate CO selectivity compared to Pd. An In$_2$O$_3$ content of 25 – 30 wt.% was required to minimize the CO selectivity of the Pt-containing samples. At a Pt/In ratio of 0.6, the catalyst with the highest Pt content of 15 wt.% showed also highest activity. The catalyst, when exposed to the feed mixture the first time after calcination but without any reduction pre-treatment, produced small amounts of methane not exceeding 1 Vol.% and decreasing to 500 ppm during steady operation. Selectivity towards carbon monoxide was remarkably low even at reaction temperatures as high as 400°C.Switching to conditions of oxidative steam reforming further increased the activity of the catalysts.

1. INTRODUCTION

Fuel processing of liquid fuels to hydrogen containing reformate appears to be a practical option for electric power generation applications based upon fuel cell technology (Kolb, 2008). Methanol is a highly suitable fuel, owing to its high energy density and its potential for future sustainable production routes.

Most research in the area of methanol steam reforming had been focused on ZnO-based catalysts such as Cu/ZnO and Pd/ZnO which exhibit relatively high activity and selectivity. However, both catalyst types present some significant disadvantages. Cu based catalysts show pyrophoric nature on exposure to oxidizing environments and the tendency of copper sintering and deactivation at elevated temperature above 300°C. Pd/ZnO-based catalysts are higher in activity, less sensitive and show low carbon monoxide selectivity (Chin et al., 2002, Chin et al., 2003). Extensive research performed by the authors of the current paper had revealed that the Pd/ZnO- catalytic system is very sensitive to the preparation technique and the danger of metallic palladium formation is high. The latter generates significant amounts of carbon monoxide then. Consequently, the search for alternative catalyst formulations to overcome these drawbacks has been the focus of the recent studies. It was found that Pd/In$_2$O$_3$/Al$_2$O$_3$ catalysts are promising and highly active candidates (Men et al., 2010, Men et al., 2009). Further investigations revealed, that Pt/In$_2$O$_3$/Al$_2$O$_3$ catalysts are even more active and show more than ten times higher activity compared to Cu-based systems. Therefore Pt/In$_2$O$_3$/Al$_2$O$_3$ catalysts are the subject of the work presented here. Catalysts of high activity are crucial for the application in catalytic wall (micro)-reactors, because the amount of catalyst coated onto the channel walls is limited. It has to be emphasized, however, that catalyst cost is a minor issue in wall coated reactors, because the catalyst utilization is much better compared to fixed beds, where diffusion limitations make higher catalyst loadings mandatory.

2. EXPERIMENTAL

Micro-structured stainless steel sheets were coated with alumina carrier material. Catalysts were prepared by initially wash-coating alumina onto the micro-channels stainless steel sheets according to a procedure described elsewhere (Zapf et al., 2003). After drying at room temperature and calcination at a temperature of 600°C in air,

the alumina carrier coating was then impregnated with the desired amount of precursor (noble metal salt solutions). After another drying step, the coatings were calcined in air for 6 hrs at 350°C. For validation purposes, the amount of the catalyst loaded onto the micro-channel was then determined by measuring the weight gain after calcination. The chemical composition and specific surface area of the catalysts discussed here is provided in Table 1. The catalysts will be identified in the text below according to their target composition, e.g. Pt5In10 refers to a target composition of 5 wt.% Pt, 10 wt.% In_2O_3 (8.27 wt.% In), balance alumina. It is obvious that the extremely high noble metal loadings lead to a decrease of the overall surface area of the samples.

Table 1: Chemical composition and specific surface area of the catalysts under investigation

	Spec. SA [m^2/g]	Elemental analysis via XRF [wt. %]		Target Composition [wt. %]	
Pd15In30	115	N/A			
Pt5In10	148	Pt: 5.74 ± 0.17	, In: 8.39 ± 0.25	Pt: 5	, In: 8.27
Pt10In10	122	Pt: 10.61 ± 0.32	, In: 8.06 ± 0.24	Pt: 10	, In: 8.27
Pt10In20	114	Pt: 10.09 ± 0.30	, In: 15.68 ± 0.47	Pt: 10	, In: 16.54
Pt10In30	102	Pt: 9.77 ± 0.29	, In: 22.40 ± 0.70	Pt: 10	, In: 24.81
Pt10In35	102	N/A			
Pt15In25	94	Pt: 13.98 ± 0.41	, In: 18.01 ± 0.54	Pt: 15	, In: 20.68
Pt15In30	89	Pt: 14.00 ± 0.42	, In: 21.60 ± 0.60	Pt: 15	, In: 24.81

Methanol steam reforming was carried out on various PdIn and PtIn catalysts in a flow-type apparatus with a micro-channel reactor at atmospheric pressure and a temperature range from 325°C to 450°C, which has been described in detail elsewhere (Kolb et al., 2004). The sandwich-type testing reactors applied are composed of two micro-structured platelets being attached face to face, each platelet carrying 14 channels with the dimension of 25 mm length, 500 μm width and 250 μm depth. Each pair of platelets was sealed by laser welding. The catalysts were not pre-reduced in hydrogen prior to the catalytic test. The high heat transfer of the micro-structured reactor allows for the investigation of gas phase reaction under isothermal conditions (Kolb et al., 2004). Methanol was premixed with water (distilled and de-ionized) at a molecular ratio (Steam to Carbon ratio, S/C) of 1.5 and fed continuously using a pressurized liquid container and a commercial liquid flow meter. Conditions of oxidative steam reforming (OSR) were adjusted by adding air to the feed with a thermal mass flow meter so as to achieve an atomic O/C ratio of 0.15. The liquid fuels were evaporated within a micro-channel evaporator. The composition of reactor effluents was analyzed by an on-line Quadrupol mass spectrometer GAM400 of InProcess Instruments, which reported averaged results every second.

3. RESULTS

Most of the experiments discussed below were performed under conditions of steam reforming (STR) at a S/C ratio of 1.5:
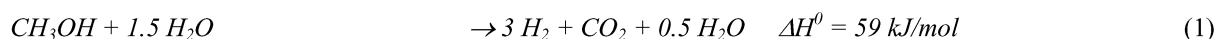
$$CH_3OH + 1.5\ H_2O \qquad\qquad \rightarrow 3\ H_2 + CO_2 + 0.5\ H_2O \quad \Delta H^0 = 59\ kJ/mol \qquad\qquad (1)$$

Figure 1 shows a comparison of the performance of a catalyst containing 15 wt.% Pd and 30 wt% In_2O_3, which had been identified as optimum composition in previous work (Men et al., 2010), with another sample which contains the same amount of Pt instead of Pd. It is obvious that the introduction of Pt increases the activity dramatically. Full conversion is achieved at about 100 K lower reaction temperature. This is accompanied by a higher tendency towards carbon monoxide formation. However, the carbon monoxide values found in the effluent remained below 1.5 vol.%, which is still acceptable for state-of-the-art high temperature PEM fuel cells. Based upon these promising results, further optimization of the catalyst composition was performed, which will be described below.
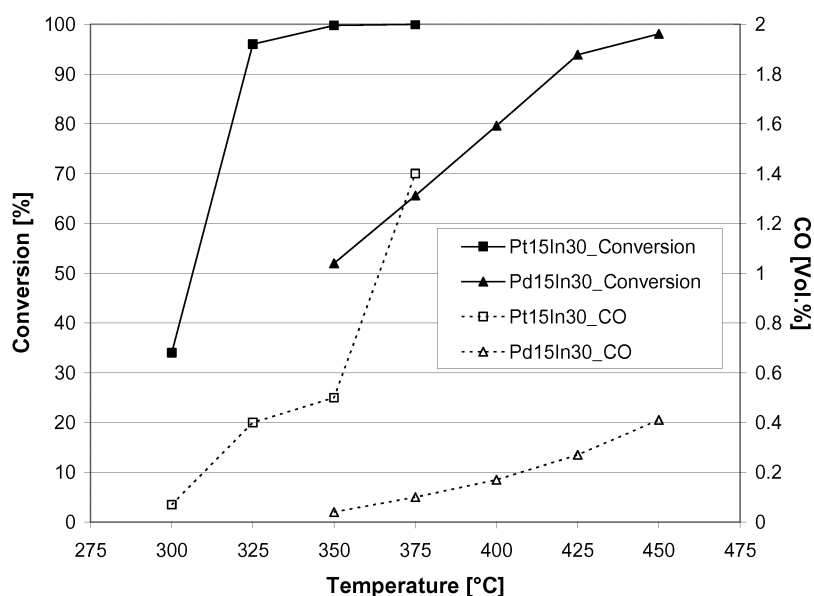
Figure 1: Comparison of methanol conversion and CO content as determined in the product over two catalysts containing 15 wt.% Pt and Pd respectively and 30 wt.% In$_2$O$_3$ under conditions of STR; S/C ratio 1.5 in both cases; feed flow rate 30 mL/min.

Figure 2 shows the carbon monoxide content as determined in the product formed over samples with varying content of In$_2$O$_3$. It is obvious, that both for samples containing 10 wt.% Pt and 15 wt.% Pt, the content of In$_2$O$_3$ reaches an optimum around 25-30 %. Above these values, no further reduction of the carbon monoxide content could be achieved. This is in line with former observations, which revealed that a certain surplus of the atomic content of Pd is required to avoid the formation of metallic Pd (Men et al., 2010). It is therefore assumed that similar to PdInAl catalysts an alloy is formed between Pt and In, which markedly alters the nature of Pt. While pure Pt is selective for methanol decomposition, the contact with In steers the catalytic function towards methanol steam reforming.

However, while it had been possible to detect a PdIn phase by XRD in former work, no evidence could be found for any bimetallic phase formation between Pt and In in the case of current samples. Further investigations are required to clarify this issue.

Figure 3 shows the methanol conversion over Pt/In$_2$O$_3$/Al$_2$O3 catalyst with three different Pt:In ratios (constant Pt loading of 15 wt.%; VHSV=48.6 L/(g$_{cat}$ h)) in the temperature range. It was found that methanol conversion goes through a maximum with decreasing Pt:In ratio, while the selectivity towards carbon monoxide is accompanied with a drastic increase in CO content from 1.4 Vol.% to 10.6 Vol.%, i.e. decreased carbon dioxide selectivity with increasing Pt:In ratio, suggesting that the composition of PtInAl catalysts determines both the surface reactivity and selectivity as already indicated above. 0.6 is the optimized Pt:In ratio to minimize the content of carbon monoxide in the product. The carbon monoxide content is much lower than predicted by the thermodynamic equilibrium of the water-gas shift reaction over the PtInAl catalyst for the product mixture of methanol steam reforming, suggesting a predominant reforming reaction pathway towards carbon dioxide.

Figure 4 shows the conversion and CO content as determined in the product formed over samples with increasing content of Pt and In at constant Pt/In ratio of 0.6. It is obvious, that the catalyst with the highest noble metal content also shows the highest activity and lowest CO formation.
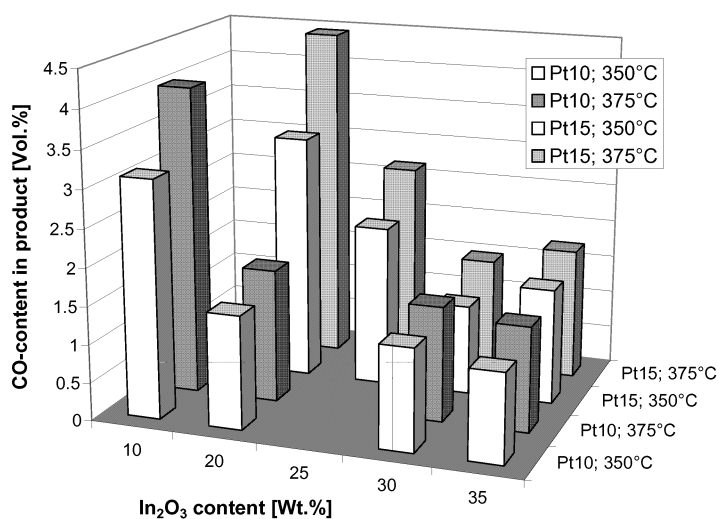
Figure 2: Comparison of CO content as determined in the product over catalysts containing 10 and 15 wt.% Pt respectively and different amounts of In_2O_3 under conditions of STR; S/C ratio 1.5 in both cases; feed flow rate 90 mL/min; conversion was complete (>97 %) in all cases.
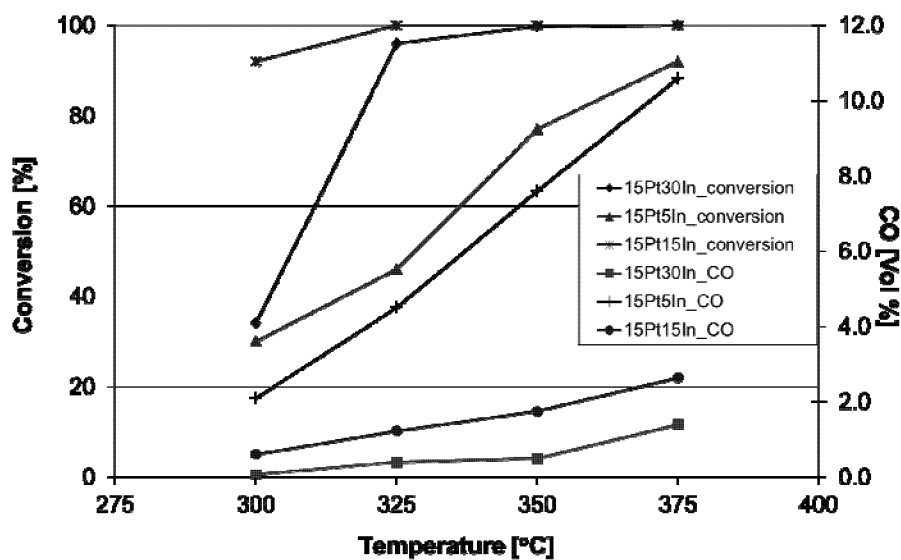

Figure 3: Comparison of methanol conversion and CO content as determined in the product over catalysts containing 15 Wt.% Pt and different amounts of In_2O_3 under conditions of STR; S/C ratio 1.5 in all cases; feed flow rate 90 mL/min.

The dynamic measurement shown in Figure 5 illustrates the behaviour of fresh (as calcined) Pt/In$_2$O$_3$ catalyst when exposed to the conditions of methanol steam reforming for the first timea dn without any further pre-treatment such as reduction in hydrogen. The fresh catalyst shows incomplete conversion which then quickly increases while the catalyst is reduced in-situ in the reaction mixture. After 30 min the conversion is in the range of 99%. Initially the catalyst generates a significant amount of methane of more than 1 Vol.% in the product mixture, which decreases after less than 10 min to values below 500 ppm. This low selectivity towards methane is not a practical problem for a future system, because methane is not harmful for all kind of PEM fuel cells in the concentration range up to 5 Vol.% (Kolb, 2008).. When increasing the VHSV stepwise, the conversion slightly decreases. At the highest VHSV of 250.4 L/(h g$_{cat}$) the conversion is still in the range of 95%, which corresponds to about 1 Vol% of methanol in the product mixture. This value is still acceptable for PEM fuel cells as mentioned previously. Similar to the Pd/In$_2$O$_3$ catalyst investigated in a previous paper (Men et al., 2010) the catalyst shows no significant increase of the selectivity towards carbon monoxide when decreasing the VHSV resp. the feed flow rate. As shown in Figure 5 the carbon monoxide concentration remains always below 1 Vol % regardless of the feed VHSV. This is a significant difference compared to conventional Cu/ZnO catalysts, which show much higher selectivity towards carbon monoxide owing to their activity for the reverse water-gas shift reaction in the absence of methanol at partial load.
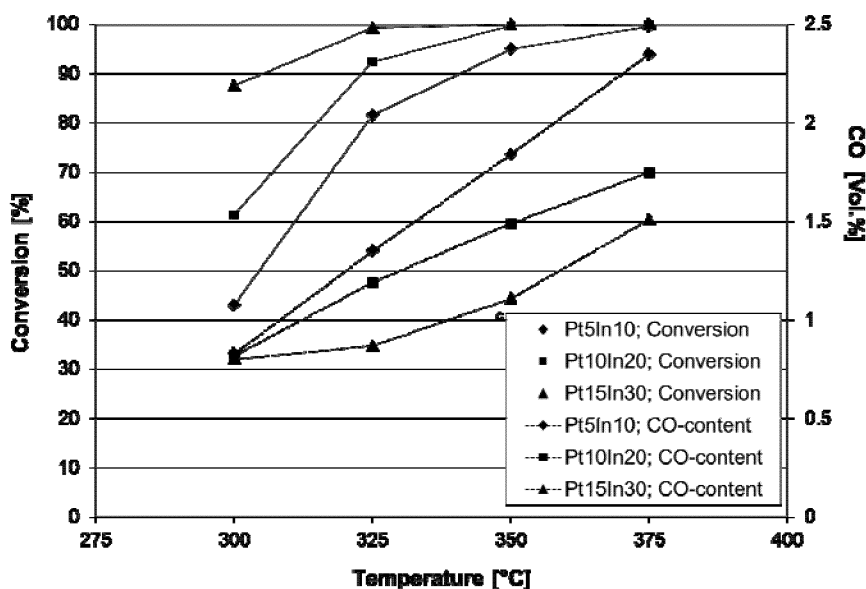

Figure 4: Comparison of methanol conversion and CO content as determined in the product over catalysts containing different amounts of Pt and In$_2$O$_3$ under conditions of STR; S/C ratio 1.5 in both cases; feed flow rate 90 mL/min.

Figure 6 shows a temperature programmed reaction over the Pt/In$_2$O$_3$ catalyst in the temperature range between 150°C and 400°C. Two upsets of the dosing equipment at 180°C and 340°C disturbed the measurements. Significant methanol conversion started at 180°C while some minor carbon monoxide formation in the range of 250 ppm was observed at lower temperatures already, possibly originating from initial methanol decomposition. Conversion then increased steadily with increasing reaction temperature, until more than 99% conversion were achieved at the final reaction temperature of 400°C. The content of carbon monoxide remained low around 250 ppm up to 300°C reaction temperature and then increased significantly. A concentration of about 1,400 ppm was

observed at 400°C reaction temperature. The methane concentration was, apart from a limited number of flyers generated by the analysis instrument, always well below 100 ppm.
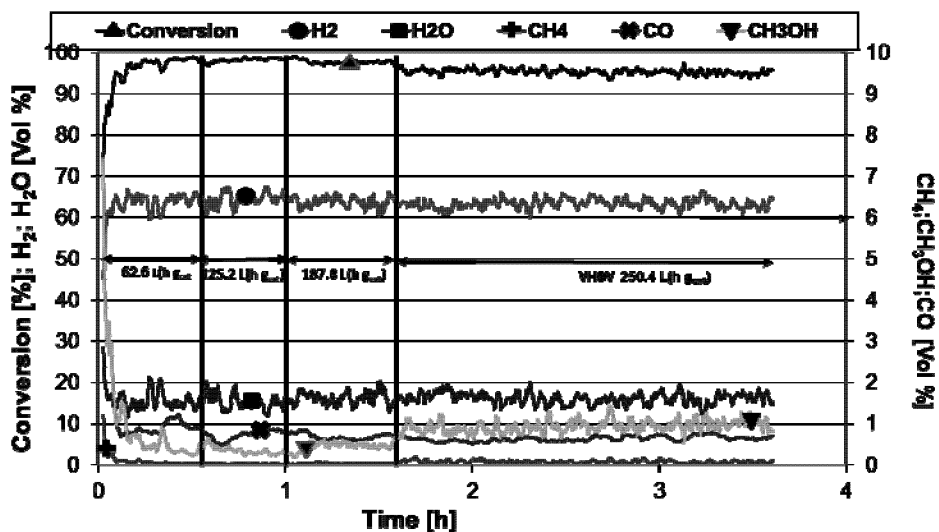

Figure 5: Conversion and product composition over as calcined Pt/In/Al$_2$O$_3$ catalyst (15 wt.% Pt, 30 wt.% In$_2$O$_3$) at different VHSV; S/C-ratio 1.5; reaction temperature 375°C; the VHSV value of 250.4 L/(h g$_{cat}$) corresponds to a feed flow rate of 120 ml/min
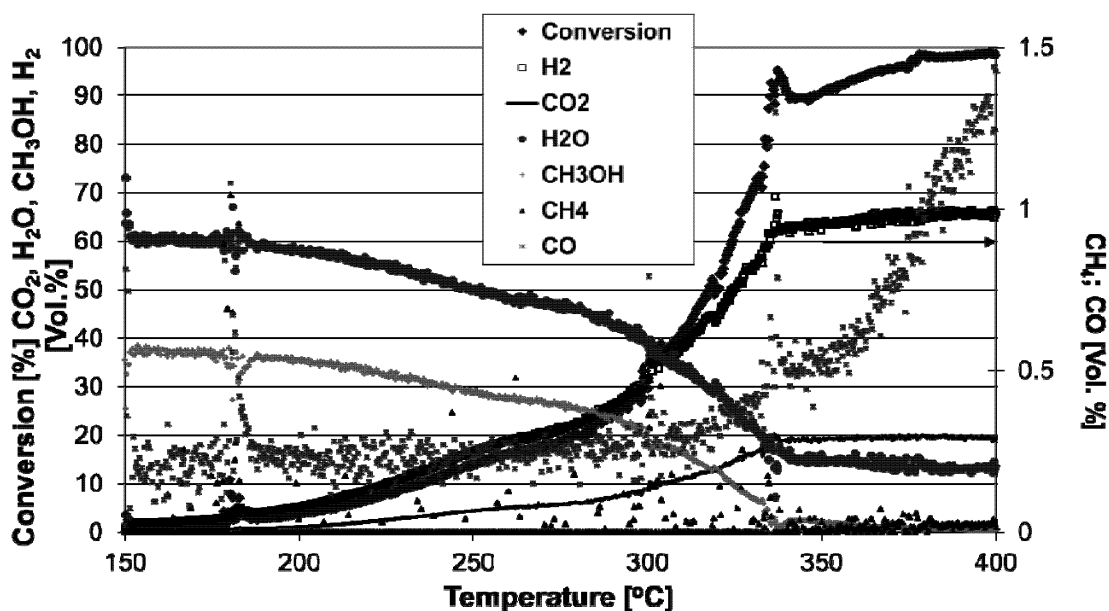

Figure 6: Conversion and product composition during temperature programmed reaction over Pt/In/Al$_2$O$_3$ catalyst (15 wt.% Pt, 30 wt.% In$_2$O$_3$) at different VHSV= 250.4 L/(h g$_{cat}$); S/C-ratio 1.5

The question arose, if the high activity of the Pt15In30 catalyst could be further increased by switching from conditions of steam reforming to those of oxidative steam reforming (OSR):

$$CH_3OH + 1.5\ H_2O + 0.075\ O_2 \rightarrow 2.85\ H_2 + CO_2 + 0.65\ H_2O\ \Delta H^{573} = +\ 24\ kJ/mol \tag{2}$$
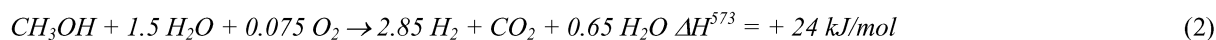
A small amount of oxygen is added to the feed, however, less than would be required for a self sustaining operation of the reaction (autothermal reforming):
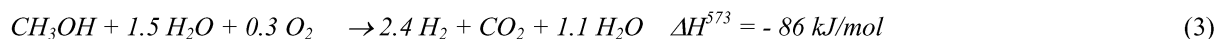
$$CH_3OH + 1.5\ H_2O + 0.3\ O_2 \quad \rightarrow 2.4\ H_2 + CO_2 + 1.1\ H_2O \quad \Delta H^{573} = -\ 86\ kJ/mol \tag{3}$$

Figure 7 shows that the activity gain from switching to conditions of OSR was only incremental, while the CO content in the reformate could be further suppressed.

Besides carbon oxides no other carbon containing species were detected apart from methane, which was formed in small amounts below 0.1 vol.% even at the highest reaction temperature over the sample under conditions of STR and OSR.
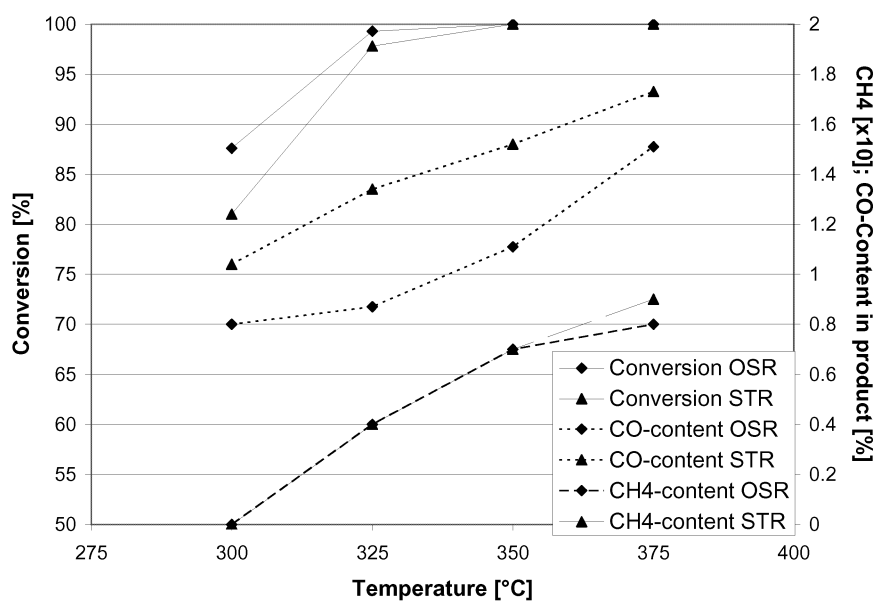

Figure 7: Comparison of methanol conversion and CO content as determined in the product over a catalyst containing 15 wt.% Pt and 30 wt.% In_2O_3 under conditions of STR (O/C = 0) and OSR (O/C = 0.15); S/C ratio 1.5 in both cases; feed flow rate 90 mL/min.

4. CONCLUSIONS

Methanol steam reforming was performed over various alumina supported PtIn catalysts within a micro-structured reactor under conditions of STR and OSR without any pre-reduction treatments. It was found that the catalytic performance of PtInAl catalysts is markedly affected by the Pt and In_2O_3 loading. The difference in catalytic activity and selectivity among these PtInAl catalysts was interpreted in terms of their different platinum

and indium interactions. A critical atomic Pt:In ratio of 0.6 was determined, below which PtInAl catalysts are very selective for CO_2 and low CO concentration of 1.5 vol.% can be easily produced. It is assumed that the active phase of methanol steam reforming is Pt in intimate contact with In_2O_3, presumably in the form of Pt-In alloy in this study. However, no evidence could be found for such an alloy to date. PtInAl catalysts have a high potential for future application in fuel processing. They show a remarkably low selectivity towards carbon monoxide at partial load. The fresh catalyst initially produces low amounts of methane, which decrease after less than 10 min and reach values as low as 500 ppm under stable operation.

5. REFERENCES

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