

Development of Micro-structured Catalytic Wall Reactors for Hydrogen Production by Methanol Steam Reforming over Novel Pt/In₂O₃/Al₂O₃ Catalysts

Gunther Kolb*, Steffen Keller, Sascha Pecov, Helmut Pennemann, Ralf Zapf

Institut für Mikrotechnik Mainz GmbH (IMM), Energy Technology and Catalysis Department,
Carl-Zeiss-Str.18-20, D-55129 Mainz, Germany
Kolb@imm-mainz.de

Methanol steam reforming was investigated over novel Pd/In₂O₃/Al₂O₃ and Pt/In₂O₃/Al₂O₃ catalysts coated into microchannels. The investigations revealed, that Pt is much more active at still moderate CO selectivity compared to Pd. An In₂O₃ 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. Switching to conditions of oxidative steam reforming further increased the activity of the catalysts.

1. Introduction

Fuel processing of liquid fuels to hydrogen containing reformat 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/In₂O₃/Al₂O₃ catalysts are promising and highly active candidates (Men et al., 2010, Men et al., 2009). Further investigations revealed, that Pt/In₂O₃/Al₂O₃ catalysts are even more active and show more than ten times higher activity compared to Cu-based systems. Therefore Pt/In₂O₃/Al₂O₃ 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.% In₂O₃ (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 Quadrupole 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:

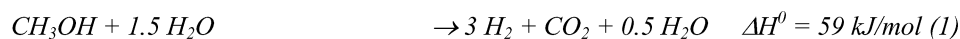


Figure 1 shows a comparison of the performance of a catalyst containing 15 wt.% Pd and 30 wt.% In_2O_3 , which had been identified as optimum composition in previous work (Men et al., 2010), with another sample which contains the same amount of Pt instead of Pd. It is obvious that the introduction of Pt increases the activity dramatically. Full conversion is achieved at about 100 K lower reaction temperature. This is accompanied by a higher tendency towards CO formation. However, the CO 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.

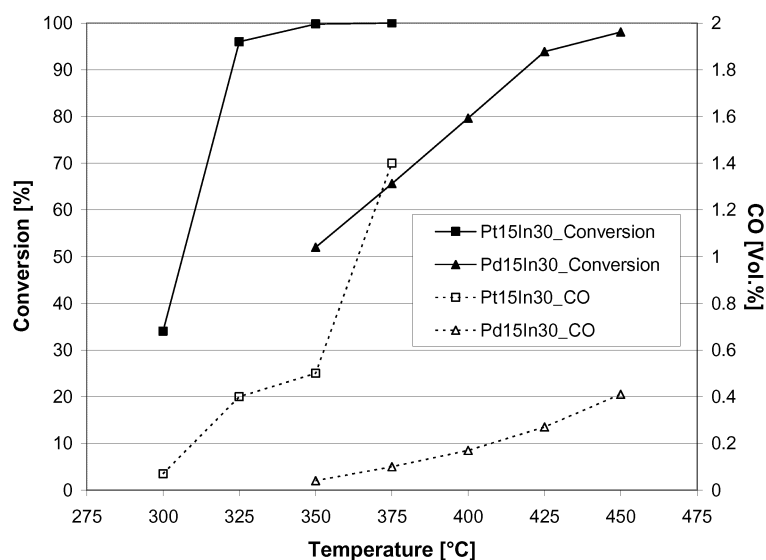


Figure 1: Comparison of methanol conversion and CO content as determined in the product over two catalysts containing 15 wt.% Pt and Pd respectively and 30 wt.% In_2O_3 under conditions of STR; S/C ratio 1.5 in both cases; feed flow rate 30 mL/min.

Figure 2 shows the CO content as determined in the product formed over samples with varying content of In_2O_3 . It is obvious, that both for samples containing 10 wt.% Pt and 15 wt.% Pt, the content of In_2O_3 reaches an optimum around 25-30 %. Above these values, no further reduction of the CO 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.

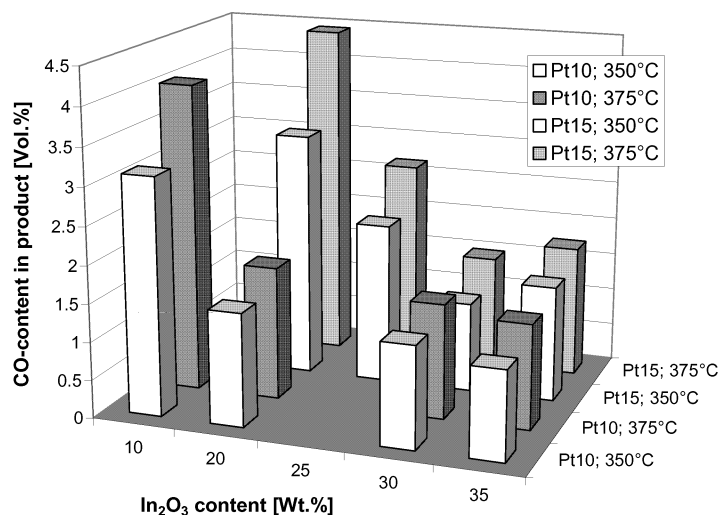
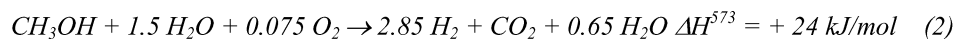


Figure 2: Comparison of CO content as determined in the product over catalysts containing 10 and 15 wt.% Pt respectively and different amounts of In_2O_3 under conditions of STR; S/C ratio 1.5 in both cases; feed flow rate 90 mL/min; conversion was complete (>97 %) in all cases.

Figure 3 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.

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):



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):

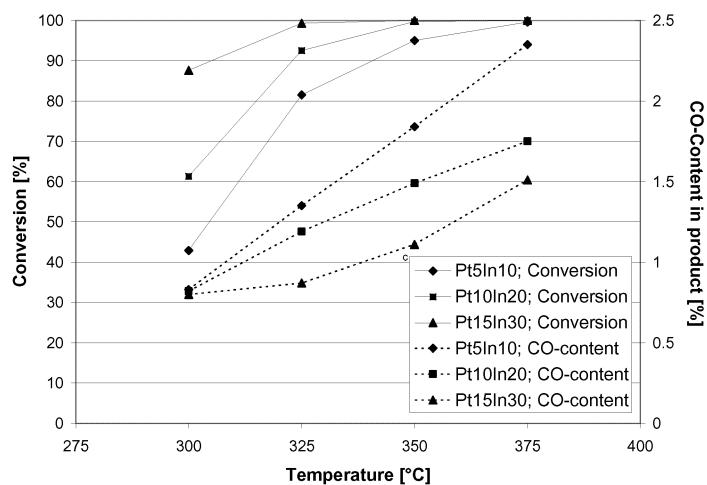
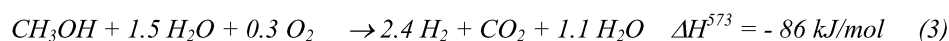


Figure 3: Comparison of methanol conversion and CO content as determined in the product over catalysts containing different amounts of Pt and In_2O_3 under conditions of STR; S/C ratio 1.5 in both cases; feed flow rate 90 mL/min.

Figure 4 shows that the activity gain from switching to conditions of OSR was only incremental, while the CO content in the reformat 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. However, methane is not harmful for PEM fuel cells up to values of 5 vol.% in the reformat (Kolb, 2008).

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.

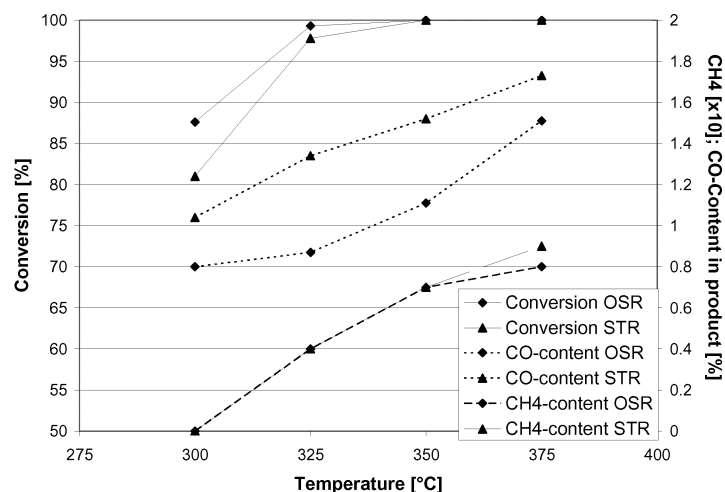


Figure 4: Comparison of methanol conversion and CO content as determined in the product over a catalyst containing 15 wt.% Pt and 30 wt.% In_2O_3 under conditions of STR ($\text{O}/\text{C} = 0$) and OSR ($\text{O}/\text{C} = 0.15$); S/C ratio 1.5 in both cases; feed flow rate 90 mL/min.

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