PREPARATION OF Pd/Zn/ZnO CATALYSTS FOR METHANOL STEAMREFORMING BY MOCVD

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Pd/Zn/ZnO catalysts in form of PdZn alloy show high activity in methanol steamreforming according equation 1 which is a promising opportunity for onboard hydrogen generation especially in the field of fuel cell technology.

$$CH_3OH + H_2O \longrightarrow 3\,H_2 + CO_2 \qquad [1]$$

Methanol steamreforming features significant advantages for mobile applications, where storage and safety aspects related with hydrogen cause serious problems.

While Pd itself only decomposes methanol to carbon monoxide and hydrogen, PdZn alloy, e.g. prepared by conventional wet impregnation technique and reductive activation, shows high activity and selectivity in methanol steamreforming towards carbon dioxide and hydrogen.

In our study Pd/Zn/ZnO catalysts are prepared on compact ceramic and powdered ZnO supports using MOCVD from from $Pd(hfac)_2$ and $Zn(ac)_2$.

The deposited films are characterized with regard to their surface morphology (SEM), composition (ESCA, ICP-AES), microstructure (XRD) and alloy formation (TPR)

Deposition parameters for the individual components Pd and ZnO were first optimized on ceramic supports. Fig. 1 shows exemplarily the variation of mean residence time τ for deposition of Pd on ceramic supports.

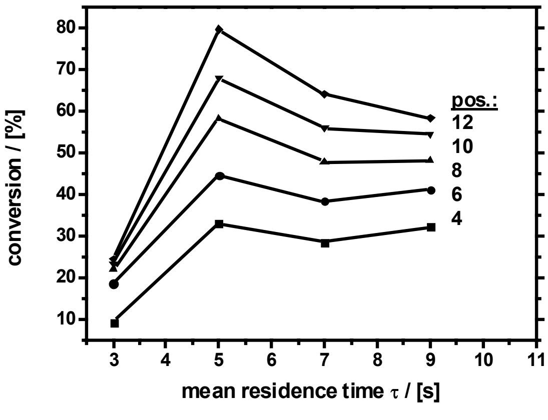

Fig. 1: Conversion of Pd precursor as a function of the mean residence time at different positions in the reactor.

The addition of hydrogen as reactive gas for the removal of residual carbon in the film was investigated. Under the reaction conditions applied in our studies instantaneous reaction occurred and furthermore against our expectation even lower Pd/C were found.

Powdered ZnO was used as support for preparation of Pd/Zn/ZnO catalysts using fluidized bed MOCVD. Commercially available ZnO (Alfa Aesar, 99%) consists of primary particles (approx. 100 nm) forming agglomerates with a mean particle size of 23 µm. Since referring to the classification proposed by Geldart, the ZnO belongs to group C powders, i.e. cohesive powders which are difficult to fluidize, a pneumatic vibrator has been applied to improve the fluidization process.

Formation of PdZn alloy is traced for the powdered samples using XRD and temperature programmed reduction (TPR). Figure 2 shows the TPR run of a Pd coated ZnO sample in comparison to the uncoated ZnO powder.

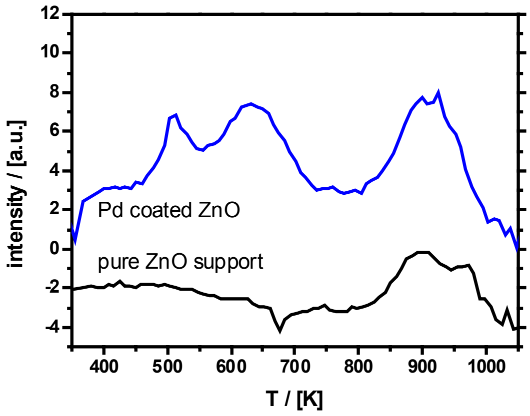

Fig. 2: TPR of Pd coated ZnO powder in comparison to pure ZnO support.

Furthermore, XRD analysis is performed after reduction treatment according to the two observed reduction steps (Figure 3).

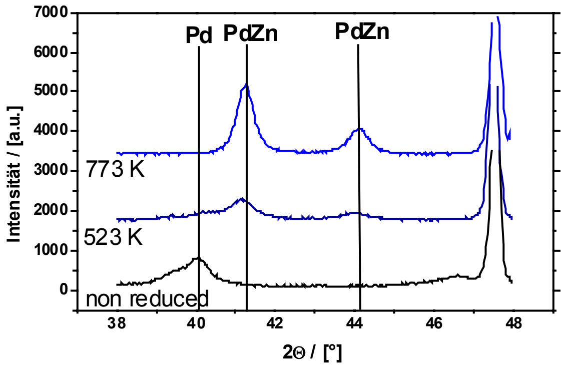

Fig. 3: XRD of Pd coated ZnO samples after stepwise reduction according to TPR peaks.

It could be shown, that both peaks of the TPR are related to the formation of PdZn alloy. TPR and XRD show consistently the formation of PdZn alloy in the temperature range between 450 K and 750 K. Stepwise emersion of the corresponding reflexes could be proved in XRD.

The aim of this study is on the one hand to produce highly active and selective catalysts with an optimum dispersion of the active noble metal and on the other hand to prepare a variety of diverse catalysts, i.e. to influence the catalytic properties by variation of the deposition parameters.