DME as a hydrogen carrier in auxiliary power systems: Development of Pd-based reforming catalysts

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Introduction
Dimethyl ether (DME), synthesized from renewable resources, has been suggested as an energy source for the future transport sector. DME is an interesting fuel candidate, both as a diesel engine fuel and as a hydrogen carrier for fuel cells. This work focuses on hydrogen generation from DME for fuel cell auxiliary power units (FC-APUs) onboard DME trucks. The development of catalysts for autothermal reforming (ATR) of DME, from small-scale screening and characterization to full scale testing, is presented in this paper. The work described has been performed within the framework of the program “Aftertreatment and fuel upgrading system of DME-fuelled diesel engines” (2005-2007) financed by the Swedish Agency for Innovation Systems, the Swedish Road Administration and the Swedish Environmental Protection Agency [1-2]. The overall vision of the project was to develop a system meeting the demands on alternative and more sustainable transport solutions in Sweden. The system combines lean combustion of DME for propulsion of the truck with NOx aftertreatment and an FC-APU.

Materials and Methods
Pd-based catalysts deposited onto 400 cpsi cordierite monoliths have been tested for autothermal reforming of DME. A screening of different supports, preparation methods and active metal loadings, as well as optimization of operating parameters during reaction, was performed at small scale (monolith dimensions 20 mm diameter, 35 mm length). Further, larger scale experiments were performed in a reactor designed to generate hydrogen for a 5 kW fuel cell in an auxiliary power unit. Operating conditions have been varied between O2:DME=0.25 and 0.9, H2O:DME=0-3, T=250-450 °C, GHSV=7500-15000 h⁻¹. A number of characterization techniques have also been performed to evaluate the properties of the materials, e.g. XRD, BET, TEM, NH3-TPD, and TPR.

Results and Discussion
Pd-based catalysts were shown to be highly effective in autothermal reforming of DME at temperatures around 400 °C. However, as the steam reforming of DME proceeds via methanol which is known to decompose over metallic Pd, the concentration of CO was high. By adding Zn to Pd catalysts, the selectivities of the reactions were shifted towards reforming which resulted in high selectivity to CO2. A number of characterization techniques have been used to elucidate the role of the PdZn alloys and the properties of the support in order to further optimize the catalyst. Mixtures of ZnO, ZnAl2O4, and Al2O3 are suggested as supports for Pd, with the possibility to provide a DME ATR catalyst with activity for all desired reactions.

Further, mapping of the operating conditions has been performed to locate regions with high hydrogen and carbon dioxide selectivity [3]. Finally, experiments at full scale have demonstrated the feasibility of DME ATR for use in fuel cell auxiliary power units onboard trucks [4]. Example of results from DME ATR over a PdZn-based catalyst is shown in Fig. 1. A low reforming temperature together with the low concentration of CO, means the complexity of the overall fuel processor will be lower compared to for example a diesel-fuelled fuel processor. Running on DME, only a few cleanup steps after the ATR will be necessary. This has been demonstrated experimentally using a simulated DME reformate over a Pt/CeO2 water-gas shift catalyst. CO concentrations of only 0.5 % after the water-gas shift step indicate that there is large potential to obtain a very compact system. If a high-temperature PEM can be used, the gas from this WGS unit could be fed directly to the fuel cell.

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