Towards an efficient process for small-scale, decentralized conversion of methane to synthesis gas or hydrogen

Dirk Neumann, Mark Kirchhoff, and Götz Veser[*]

Department of Chemical Engineering
1249 Benedum Hall, University of Pittsburgh
Pittsburgh, PA 15261, USA

Introduction

Methane is one of the major contributing gases to global warming. According to a recent study by the IPCC [1], about 70% of all atmospheric methane is of anthropogenic origin, and this value has shown a particularly strong growth rate through the 1990s with an average increase of about 7 ppt/yr. However, since methane has a very short atmospheric lifetime of about 8 – 12 years, it also appears to be one of the most promising greenhouse gases for short-term measures to counter global warming trends with (almost) immediate impact [2].

In the US, more than a third of all methane emissions result from landfills [3]. These emissions not only represent a significant environmental problem, but at the same time also are a waste of a valuable and renewable natural resource. However, these sources are too small and often too remote to be exploited with existing industrial technology for methane utilization (other than combustion). With current trends towards a more sustainable economic growth and a clean, hydrogen-based economy, however, it seems necessary to develop technologies for efficient, small-scale and decentralized utilization of these and similar methane resources.

Direct 'valorization' of methane, i.e. the direct conversion of methane to higher value products via process routes such as methane coupling, is currently neither efficient nor economical. The only available route for methane valorization is therefore the indirect route via the production of synthesis gas, a mixture of CO and hydrogen, followed by secondary processes such as methanol or Fischer-Tropsch syntheses. In these indirect processes, the syngas production step is currently the limiting factor particularly for small-scale processes, with about 60% of overall investment costs.

Catalytic partial oxidation (CPO) of methane to synthesis gas has recently found much attention as alternative to the industrially dominant, highly endothermic steam reforming route ($CH_4 + H_2O$ B $CO + 3\ H_2$, $\Delta H_R = 206$ kJ/mol). CPO is a mildly exothermic reaction and has thus the potential to be run autothermally ($CH_4 + 0.5\ O_2$ B $CO + 2\ H_2$, $\Delta H_R = -36$ kJ/mol). This independence on external heat sources is quintessential for an efficient small-scale, decentralized process. Furthermore, the reaction is characterized by the extremely high reaction rates typical for catalytic oxidation processes at high temperatures ($T > 800^oC$). This allows for catalytic contact times in the order of about 10 ms and thus for extremely compact reactors with large through-puts.

However, for all its advantages over the conventional steam-reforming route, adiabatic CPO of methane is far from optimal. Simple thermodynamic calculations demonstrate that adiabatic temperatures are too low to achieve optimal methane conversions and syngas selectivities, and even these adiabatic temperatures are only achieved via internal combustion of some of the methane feed, hence intrinsically capping the maximum attainable yields at autothermal process conditions [4].

However, combining the CPO reaction route with an efficient heat-integrated reactor concept, a very efficient overall process can be attained. In this report, we briefly present some of our recent results on CPO of methane in a catalytic reactor with integrated regenerative heat-exchange via reverse-flow operation.

Experimental Set-up

The experimental set-up has been described in more detail in a previous publication [4]. The reactor consists of a stainless steel – quartz glass double tube, in which the catalyst is positioned between two extruded cordierite monoliths which serve as heat reservoirs. Four valves are positioned pair-wise on either end of the reactor to allow switching of the flow direction at reverse-flow operation. If the flow direction is reversed periodically at an appropriate frequency, the heat of the exothermic oxidation reaction is "integrated" and reactor temperatures are increased well beyond the adiabatic limit.

Moveable thermocouples allow measurement of temperature profiles, while reactant and product concentrations are measured via mass spectrometry and gas chromatography.

The catalysts used are platinum precipitated from a salt solution on an alumina foam monolith, and a novel nanocomposite catalyst, in which platinum nanoparticles are anchored in a high-temperature stabilized ceramic matrix [5].

Results and Discussion

Pt-Alumina Catalyst. Figure 1 shows results from CPO of methane with air over a platinum-coated alumina foam monolith at stationary reactor operation ('SS') and at reverse-flow operation ('RFR') versus methane/oxygen ratio. One can see that the regenerative heat-integration in the RFR leads to a significant improvement in methane conversion of about 20% over the whole range of conditions (left graph), as well as drastic improvements in hydrogen selectivity of up to 40% (right graph).

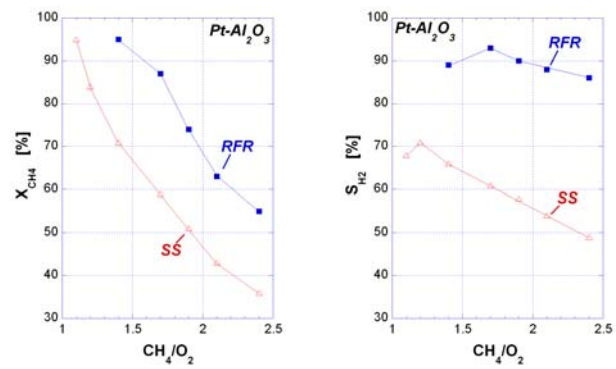

Figure 1. Experimental results for CPO of methane over an alumina supported Pt catalyst in a comparison between steady-state (SS) and reverse-flow operation (RFR). Methane conversions (left graph) and hydrogen selectivities (right graph) are shown versus methane/ oxygen-ratio at a reactor feed of 4 slm methane/air. The duration of one half-period at RFR operation was 15 s.

While methane conversion increases continuously with decreasing methane/oxygen ratio due to the increasing amount of oxygen available for methane oxidation, hydrogen selectivity shows a maximum near $CH_4/O_2 = 1.2$ at SS which shifts to about $CH_4/O_2 = 1.7$ at reverse-flow operation. This maximum can be explained by the superposition of two effects: The overstoichiometric supply of oxygen for $CH_4/O_2<2.0$ leads to some total oxidation, hence reducing selectivities. At the same time, the exothermicity of the total oxidation reaction also increases temperatures and hence thermo-dynamically attainable selectivities, thus helping process selectivities. The observed shift in the maximum therefore indicates that less total oxidation is needed to achieve high reaction temperatures, as reactor temperatures are already increased due to the heat-integration. Heat-integration thus leads to an effective conversion of thermal energy (heat) into chemical energy (process yields).

Reactor Simulations. The experimental investigations were complemented by a detailed simulation study of the reaction behavior at reverse-flow operation of the reactor in order to obtain a better understanding for the reaction kinetics at high-temperature unsteady-state conditions. A heterogeneous one-dimensional reaction-diffusion reactor model was coupled with detailed reaction kinetics for the catalytic surface reaction which had previously been validated against experimental results at stationary reactor operation [6]. Figure 2 shows results from one simulation: catalyst temperatures (left graph) and water concentrations (mass fractions, right graph) in the catalyst zone are shown for one half period immediately after flow reversal.

The reactor model confirms the (qualitative) experimental observation that maximum catalyst temperatures are kept below 1500°C and thus maintain within a range. Furthermore, one can see that a strong (spatial) temperature maximum develops near the catalyst entrance which matches with the maximum in water concentration in this location. This indicates that some total combustion of methane is occurring near the catalyst entrance, the exothermicity of which results in strong temperature maxima.

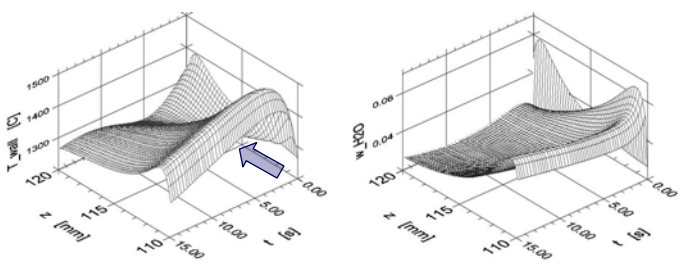

Figure 2. Simulation results for CPO of methane over a Pt catalyst at reverse-flow reactor operation. Temperature profiles in the catalyst bed (top graph) and water concentrations (mass fractions, bottom graph) are shown versus catalyst length (z) and time after flow reversal (t). Flow direction is from right to left as indicated by the arrow in the top graph. Reactor feed is methane/air at room temperature with CH_4/O_2 = 2.0 and RFR periodicity is 15 s.

At the same time, one can also see that the *temporal* temperature maximum in the catalyst zone corresponds to a *minimum* in water concentration. This is due to the (transient) increase in reaction temperature due to heat-integration which leads to an improvement in selectivity and hence to a decrease in the amount of water formed in the reaction.

This results again highlights the above mentioned complex interplay between reactor temperatures and reaction selectivity: while low selectivity results in high reactor temperatures, these high temperatures in turn improve reaction selectivity and hence counter the increasing temperatures.

Pt-BHA Nanocomposite Catalyst. As seen above, heat-integrated reactor concepts alone are not sufficient to achieve optimal reaction temperatures. Development of an efficient process should always involve reactor engineeering in combination with the design of adapted catalyst systems. We recently developed novel nano-composite catalyst systems, in which well-defined noble metal nanoparticles are embedded in a ceramic matrix, yielding highly active, selective and high-temperature stable catalyst systems [5].

Figure 3 shows experimental results in CPO of methane over a Pt-barium hexa-aluminate (Pt-BHA) nanocatalyst at stationary reactor operation ('SS') and reverse-flow operation ('RFR') with varying methane/oxygen ratio. One can see that the results both at SS and RFR are significantly improved in comparison to the conventional supported platinum catalyst (see fig. 1). Furthermore, heat-integration again leads to a strong improvement in conversions and selectivities for this catalyst, raising methane conversion at stoichiometric conditions to about 80% with hydrogen selectivities of about 95%. While this is still far from the thermodynamically allowed complete conversion at perfect selectivity, it is a drastic improvement in comparison to the values of less than 50% conversion and about 55% H_2 selectivity at conventional stationary reactor operation with a conventional catalyst.

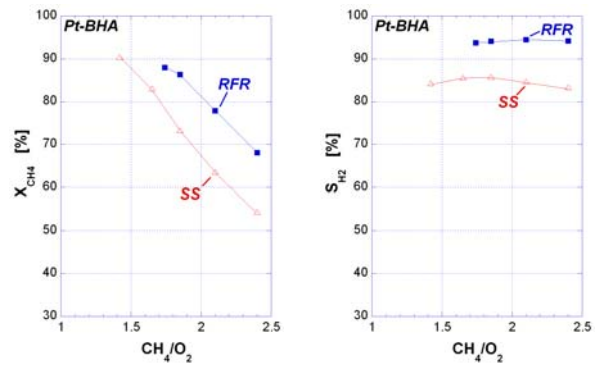

Figure 3. Experimental results for CPO of methane over a novel nanocomposite Pt-BHA catalyst in a comparison between steady-state (SS) and reverse-flow operation (RFR). Methane conversions (right graph) and hydrogen selectivities (left graph) are shown versus methane/oxygen-ratio at a reactor feed of 4 slm methane/air. The duration of one half-period at RFR operation was 15 s.

Conclusions

We presented some recent results from our ongoing studies towards the development of a flexible and efficient process for methane valorization via direct catalytic partial oxidation to synthesis gas or hydrogen.

The combination of reactor engineering with catalyst development, and of experimental investigations with numerical simulation is essential for the development of such processes which we see as critical enabling technologies for a more efficient and sustainable utilization in particular of small-scale, decentralized and remote methane resources.

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