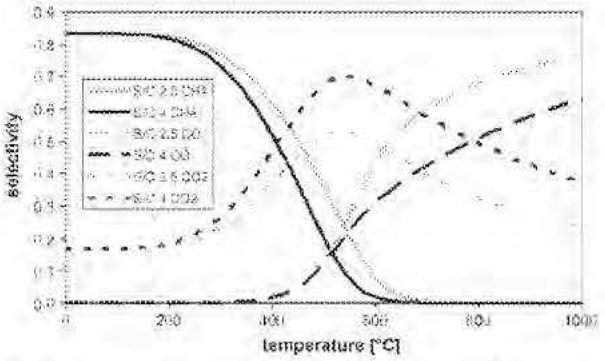

Fig. 15. Product selectivity at thermodynamic equilibrium in SR of propane.

At temperatures below 400 °C, SR of natural gas leads to a net methane production (Fig. 10). Since methane is little converted in this temperature range (Fig. 2), the selectivity is mostly determined by the higher alkanes. Compared with SR of methane as single component gas, the net conversion of methane starts at higher temperatures but increases faster with increasing temperature (Fig. 17). Below 400 °C, methane is faster formed from higher hydrocarbons than decomposed, because it is not very reactive at those low temperatures. Since, the higher hydrocarbons are converted first leading also to increased methane concentration, the S/C ratio decreases for methane and increases for the higher alkanes. Therefore, the higher hydrocarbons are not only reformed with S/C = 4 but with S/C ~7 in this temperature range. The conversion of the higher alkanes at temperatures above 450 °C is high for all S/C ratios. If one considers a minimum amount of steam for the conversion of the higher alkanes, e.g. S/C = 1, the remaining steam would increase the S/C for methane from 4 to 4.8 leading to a higher conversion compared to steam reforming of methane. The lower methane conversion in steam reforming of natural gas between 400 and 450 °C is a result of the net methane production due to the high conversion of the higher alkanes and a possibly low methane conversion.

Alkanes higher than methane are likely to react not only on the catalytic surface, but also in the gas phase. The comparison of the experimentally observed behavior of the reactor with and without catalytic coating of the monoliths (Fig. 11) reveals that alkane conversion occurs at considerably higher temperature without catalyst. The product spectrum of purely homogeneous conversion (no catalytic coating) leads to unsaturated hydrocarbons (ethylene, acetylene, propylene; composition depends on fuel, temperature, and S/C). These products could barely be found in the presence of a catalyst. Consequently, the catalyst is either not selective for them or gas-phase intermediates are adsorbed and consumed on the

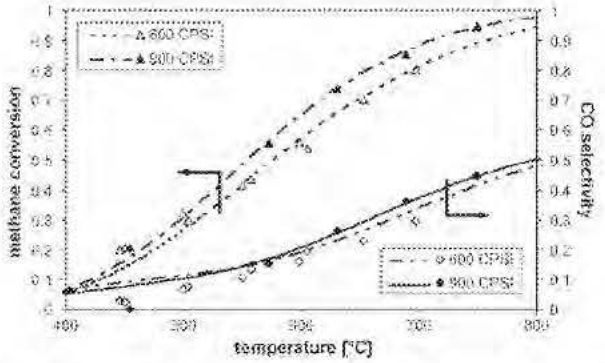

Fig. 16. Impact of channel density on methane conversion and CO selectivity in SR of methane with S/C 3.3; symbols: experiment, lines: simulation.

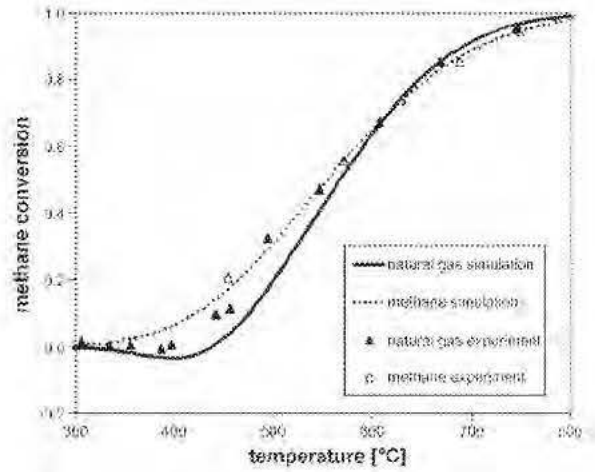

Fig. 17. Comparison of experimentally derived methane conversion in SR of natural gas (▲) and SR of methane (△); cpsi 900, S/C 2.5.

catalyst. The product distribution of the non-catalytic conversion experiments are well-predicted by the numerical simulation. The analysis of the simulation results for the catalytic system, as discussed below, reveals that at the high temperatures, at which SR by gas-phase reactions occurs, the higher alkanes are totally converted in the first region of the catalyst. Therefore, there is not enough time (length) to build-up a radical pool in the gas phase to initiate significant conversion in the gas phase, which means, the ignition delay time is larger than the lifetime of the higher alkanes in the catalyst. Actually, to fully understand the interaction between gas phase and surface reactions one needs to include adsorption and desorption of radicals in the surface reaction mechanism. However, as the results and discussion above shows these steps are not significant for the catalyst considered here.

The yield of hydrogen depends on temperature and S/C. The yield can either be calculated for the conversion of the alkane or the conversion of alkane and water. Fig. 18 presents the yield based on the alkane conversion only. The hydrogen yield increases with increasing S/C and increasing chain-length of the alkanes. Only propane is shown as example for the higher alkanes in Fig. 18 since their curves lie closely together. The hydrogen is produced either from the steam reforming reaction or the water-gas shift. The first one remains constant as soon as full conversion is reached. The decline of the water-gas shift, indicated by the increasing

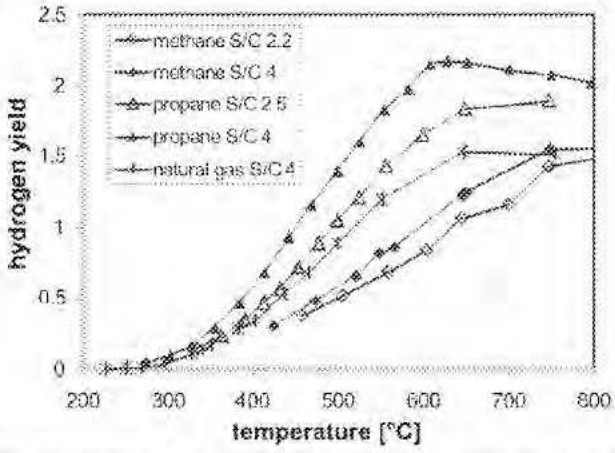

Fig. 18. Comparison of experimentally determined hydrogen yields in SR of methane with S/C 2.5 (◇) and S/C 4 (◆), steam reforming of natural gas with S/C 4 (*), steam reforming of propane with S/C 2.5 (△) and S/C 4 (▲).