

Fig. 11. Experimentally determined product yields in catalytic (catalyst with 900 cps) and homogeneous SR of propane with S/C 4; filled symbols: with catalyst; open symbols: without catalyst.

and complete conversion is reached at 900 °C. Water is only converted to a minor extent (below 5%). The product spectrum differs significantly from those of the catalytic experiments and are dominated by unsaturated hydrocarbons.

The influence of S/C is negligible due to the low water conversion. Although it would be more appropriate to call this process hydrocracking instead of steam reforming due to the low water conversion, the latter notation will still be used further on for continuity.

Only some experiments with one S/Cs per alkane and few temperatures are carried out in order to test the suitability of the chosen gas-phase mechanism. In non-catalytic SR of ethane with S/C 2.5 at 920 °C, the selectivities of the three major carbon-containing products are 50.3% C₂H₄, 29.0% C₂H₂, and 10.7% CH₄. In SR of propane with S/C 4 at 940 °C we found 41.2% C₂H₄, 26.4% CH₄, and 19.0% C₂H₂, and in SR of butane with S/C 4 at 840 °C 55.7% C₂H₄, 15.3% CH₄, and 11.7% C₃H₆. Fig. 11 shows as example propane conversion and the yield of the main products of SR of propane with S/C 4 with and without catalyst.

6. Discussion

Conversion (Figs. 2, 4, 5 and 7-9) and product selectivity (Figs. 3, 6 and 13) in steam reforming of alkanes depend on S/C. The conversion of all alkanes slightly increases with increasing S/C for a given temperature. The decreasing increments of conversion with more steam addition (Fig. 2) is caused by the thermodynamics of the system (Fig. 12). CO selectivity strongly increases with rising temperature but falls with rising S/C (Figs. 3 and 13) according to

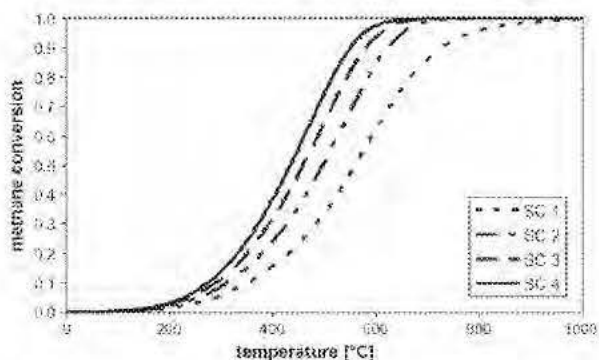


Fig. 12. Methane conversion at thermodynamic equilibrium as function of temperature for methane/steam mixtures with varying S/C.

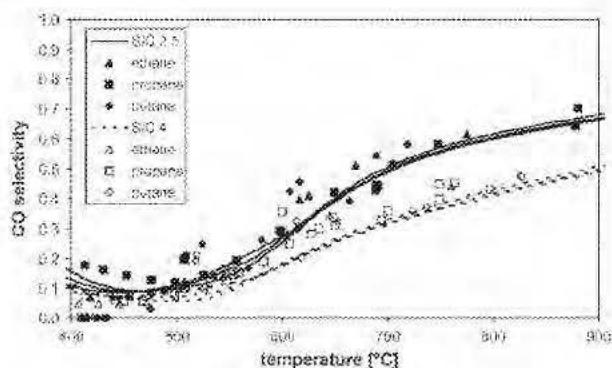


Fig. 13. CO selectivity in SR of ethane (▲), propane (■), and butane (◆); filled symbols/full lines: S/C 2.5, open symbols/dashed lines: S/C 4; symbols: experiment, lines: simulation.

the water-gas shift equilibrium:



There is little difference between ethane, propane, and butane concerning the CO selectivity as function of temperature and S/C (Fig. 13); CO selectivity actually shows a minimum at low temperatures, where methane selectivity peaks (Fig. 6). All alkanes show higher CO selectivity for lower S/C again. Both the simulation and experiment indicate no significant differences between conversion and selectivity of the individual C₂–C₄ alkanes (Fig. 14).

The temperature dependence of the selectivity is dominated by CO at high temperatures and CO₂ at low and mediocre temperatures; methane is only formed at low temperatures agreeing with the thermodynamic trends (Fig. 15). The selectivity of SR of the higher alkanes is close to the values at thermodynamic equilibrium except at temperature below 400 °C, where methane is the thermodynamically favored product. The selectivity of CO in steam reforming of methane is lower than the thermodynamic limit due to surface kinetics.

As expected, the conversion of methane increases with increasing surface to volume ratio, whereas no significant influence of the cross-section of the individual channels on selectivity is observed (Figs. 4 and 5). A catalyst with 900 cps (channels per square inch) leads to higher conversion of methane (Fig. 16) and, for temperatures exceeding 570 °C, a slightly higher CO selectivity than a 600 cps catalyst.

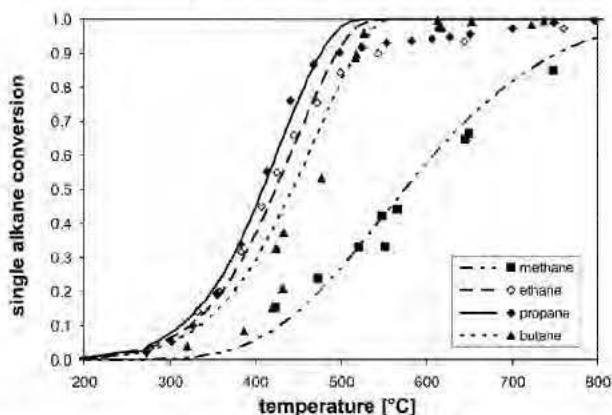


Fig. 14. Conversion of methane (■), ethane (◄), propane (◆), and butane (▲) in SR of the individual alkanes. S/C = 4; symbols: experiment, lines: simulation.